Industrial Brine Characterisation and Modelling

A Thesis submitted for the Degree of Master of Science by:

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16 May 2010

Without You Lord, I am Nothing!

This work is dedicated to my family and friend. Especially to my late family members: My Mother and role model Nobenele Getrude Zibi; my Brother and inspiration Cebiso Zibi; my Sister and diva of all time Noluyolo Woleka Zibi. You are always in my heart.

Declaration

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for another degree at any university or institution

Signed by candidate

Signature Removed
Lindizwe Mthanjiswa Zibi

16 May 2010

Executive summary

Industrial wastewater contains many soluble inorganic and organic components and solid particles. This study focused on inorganic industrial hypersaline brines. Chemical engineering presents a variety of mechanical, thermal, biological and chemical processes capable of treating hypersaline brines to the standard required by legislation. However, some of these technologies are inefficient, costly and outdated and are not applicable in solving modern brine accumulation problems. The provision of novel and viable solutions is highly dependent on research and development, which encompasses accurate wastewater characterisation and modelling for the design of wastewater treatment plants or extension of existing plants. Effective and accurate characterisation of brines is essential for accurate thermodynamic modelling, accurate experimental verification, and downstream pilot plant development.

A characterisation and modelling protocol was developed and applied to three South African brines. The principle steps in the protocol were brine sampling and storage, brine analysis and thermodynamic modelling. The chosen analytical methods were ion chromatography (IC) for anion analysis, inductively coupled plasma mass spectroscopy / inductively coupled plasma atomic emission spectroscopy (ICP-MS/ICP-AES) for cation and trace elements analysis, Total Kjeldahl Nitrogen (TKN) method for total nitrogen analysis, Gran titration method for the total alkalinity analyses respectively.

Reliable thermodynamic modelling was dependent on a comprehensive brine analysis program, which in turn was highly dependent on a well-executed brine sampling and storage program. The retention of the brine samples beyond the maximum holding period without determining pH and alkalinity could have contributed towards the resultant ion imbalance. pH had a recommended analysis time limit of 24 hours and thus could have changed by the time the brine samples got to the laboratory from their respective industrial sites. This could have caused the bicarbonate ↔ carbonic acid equilibrium to shift towards the formation of carbonic acid. This then resulted in a reduction of the overall anion charge, thus resulting in an ion imbalance. The inclusion of the carbonate system in the brine analysis contributed towards a reduction in ion imbalance.

The general methods all gave underestimates of the actual parameters when tested using synthetic brine solutions. No error was caused by the presence of other components in the complex brine matrices when conducting analysis of specific components. Dilution factors did not affect analysis

results.

The effects of brine characterisation on the recovery of salts and ice using Eutectic Freeze Crystallisation (EFC) were determined. The thermodynamic simulation was dependent on accurate brine analysis results. The carbonate system was used as a basis of testing the sensitivity of cooling crystallisation on pure salt and ice recovery. Initially the carbonate system was excluded which resulted in the simulation prediction of pure $Na_2SO_4.10H_2O$ salt forming. However, the inclusion of carbonate in the thermodynamic simulation resulted in the prediction of $Na_2CO_3.10H_2O$ salt forming, which contaminated $Na_2SO_4.10H_2O$ salt thus producing a double salt. This was useful information as it meant that seeding would be necessary to selectively recover a pure $Na_2SO_4.10H_2O$. This illustrated the importance of conducting a full brine analysis when characterising industrial inorganic hypersaline brine systems.

Acknowledgements

I would like to express my sincerest gratitude to my project supervisor, Professor A.E. Lewis and co-supervisor, Mr. J. Nathoo for giving me the opportunity to complete my Masters. Thank you for your patience and support in helping me build my research skills.

I would like to thank the Crystallization and Precipitation Unit for everything. You guys are the best and I will treasure you for the rest of my life.

I would like to thank all those that were directly and indirectly involved in my project. Special thanks to: Mr Patrick Sieas for his assistance and great water analysis work; Professor Ekama and the Civil engineering water lab crew for their invaluable assistance and allowing me to use their facilities; Sinethemba for his invaluable assistance in the CPU labs.

I wish thank my family and friends for emotional and moral support they gave me through the darkest moments of my project. To all of you, thank you! I wish to thank my Father and late Mother for everything. To my late brother, thank you for being my inspiration and the pillar of my life!

Most of all, thank you God Almighty for keeping me alive and blessing me with all of the special people in my life.

Much Love!

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Chapter 1 Introduction

South Africa is located in a water scarce region with frequent droughts that tend to last for several years at worst of times and average annual rainfall is 497 mm compared to a world average of 860 mm (Department of Water Affairs and Forestry, 2007). With the present global warming and climate change phenomena, it is not certain how the drought patterns will affect South Africa. Due to the South African population increase and economic growth, water demand is forecast to increase in the near future (Haldenwang, 2005).

Water is a crucial element in industrial processes, such as mining, refinery and gasification processes, in terms of the quantity and the quality (Pulles et al., 1996). South African industrial processes utilize approximately 20% of the countries fresh water resources. However, with the challenges of water shortage and strict environmental legislative constraints, it is essential for the water consuming industrial sector to seek methods of treating, recycling and preserving water and minimising wastewater accumulation in their respective processes (Gordon, 2001; McPhail et al., 2004; Glater and Cohen, 2003).

Industrial wastewater can contain many soluble inorganic and organic components and solid particles, depending on the industrial process. This study will focus on inorganic industrial hypersaline brines. Chemical engineering presents a variety of mechanical, thermal, biological and chemical processes capable of treating hypersaline brines to the standard required by legislation (Mersmann, 1995). However, some of these technologies are inefficient, costly and outdated and are not applicable of solving modern brine accumulation problems.

The provision of novel and viable solutions is dependent on research and development, which encompasses accurate wastewater characterisation and modelling for the design of wastewater treatment plants or extension of existing plants (Musvoto and Ramphao, 2007). Figure 1 illustrates protocol for brine treatment using eutectic freeze crystallisation (EFC) developed by Lewis et al. (2010). Effective and accurate characterisation of brines is essential for accurate thermodynamic modelling, a more effective experimental verification, and downstream pilot plant development.

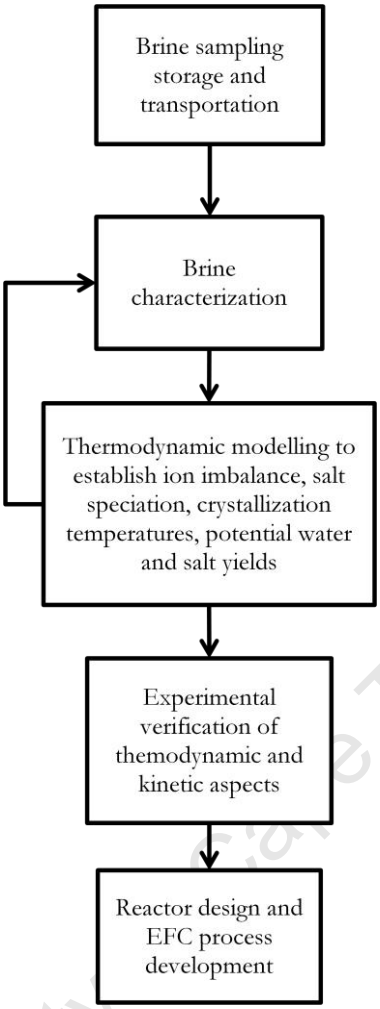

Figure 1: The protocol for brine treatment using EFC (Lewis et al., 2010)

1.1 Aim

The objectives of this project were as follows:

i. To develop inorganic hypersaline industrial brine characterisation and thermodynamic modelling protocol;

ii. To use three South African hypersaline brines as case studies: two metallurgical brine types and a gasification brine. This included conducting sampling, analysis and thermodynamic modelling on the case study brines;

iii. To determine the effects of not conducting a full brine characterisation and modelling protocol on recovery of salts and ice when using EFC as a water treatment method.

1.2 Scope of study

This project forms part of the greater EFC project conducted by the Crystallisation and Precipitation Unit (CPU) in the University of Cape Town Chemical Engineering Department headed by Professor A.E. Lewis. The case study brines that were investigated are currently case study brines used in the greater EFC project, and this project was primarily concerned with developing a protocol for characterising these case study brines.

Chapter 2 Literature Review and Theory

This chapter was structured as follows: The first part reviewed literature on the different industrial processes of the case study brines; the second reviewed literature on characterisation and modelling of industrial electrolyte systems; the third part dealt with literature on eutectic freeze crystallization (EFC). The last part dealt with the relevant aqueous chemistry theory of inorganic hypersaline brines.

2.1 Industrial brine

The identification of the sources of wastewater in industrial processes plays an important role in the water treatment process (Mersmann, 1995). This subsection presents a brief outline of brines in general, and proceeds to focus on the specific South African inorganic industrial brines from metallurgical and gasification processes. It summarizes the main sources of contaminants, and the typical concentration levels of contaminants in some of these brines found in literature.

By definition, industrial hypersaline brine is process water that contains inorganic and/or organic compounds. Globally, large volumes of industrial hypersaline brines are produced in the manufacture of chemicals such as pesticides, herbicides, polyhydric compounds, organic peroxides and pharmaceuticals (Woolard and Irvine, 1995). Brines are also generated in mining and mineral processing (Pulles et al., 1996; Forbes et al., 2000), oil and gas operations, power generation processes (van Dyk et al., 2006), agro-food processing (Lefebvre and Moletta, 2006), paper and pulp processing (Tambosi and co-workers, 2006). These brines generally contain, among other contaminants, high concentrations of salts, oil, organic acids, heavy metals, and radionuclides (Woolard and Irvine, 1995; Stephenson, 1992; Pulles, 1993).

The accumulation of untreated hypersaline brines in industrial processes is fast becoming a problem and places the environment under immense pressure. Brine accumulation is due to increase in industrial process activities driven by the growing South African economy. Waste minimization practices generate additional untreated highly concentrated brines (Woolard and Irvine, 1995). This is because purged untreated brines accumulate with time, and the complex nature of the multi-component brines makes it difficult to treat them.

High salinity industrial wastes are already generated in arid parts of the world where water is scarce and expensive (Woolard and Irvine, 1995). It is thus essential for the industrial processes to develop

novel methods of treating the brines they produce in their respective processes.

2.1.1 Metallurgical brine

South Africa is the number one producer of platinum group metals (PGMs) globally, and in 2006 it was reported that its known reserve base of PGMs represented 87.7% of the world's total. There are currently eighteen platinum producing mines and two recovery plants operating in the South African Bushveld complex (Conradie, 2007). Beneficiation of the ore through milling, flotation and smelting, to form matte is undertaken at various concentrators and smelters facilities (Conradie, 2007). Matte generally contains PGMs, gold, silver and base metals (nickel, copper and cobalt). Further refining of matte to recover base metals and constituent precious metals, by means of a hydrometallurgical refinery process, occurs at Anglo Platinum's refineries near Rustenburg, Western Platinum's refineries near Brakpan, and Impala Platinum's refineries in Springs (Conradie, 2007). According to Botha et al. (2007) the definition of hydrometallurgy the extraction and reclamation of metals from ores by treating them with aqueous chemical solutions, including extraction by electrolysis and ion exchange and the chemical solutions in hydrometallurgical processes are generally an acid or a base dissolved in water.

2.1.2 Metallurgical brine contaminants

The aim of the base metals refinery (BMR) is to remove as much of the base metals as possible and advance the Platinum Group Metals (PGM) concentrate to the precious metals refinery (PMR) circuit for further processing (Khan et al., 2009; de Beer, 2008). The principal reactions occurring in the BMR leach stage are the reactions of Ni and Ni_3S_2 with excess sulphuric acid (H_2SO_4) and Cu^{2+} in solution in the presence of oxygen to form copper sulphide and nickel sulphate (Khan et al., 2009; Rademan, 1995; Rademan and co-workers, 1999).

The aim of the PMR process is to cost-effectively separate the various platinum group metals in the PGM concentrate from the Base Metals Refinery into individually pure metals of highest commercial value. The dissolution of PGM in excess Cl_2 and HCl follows the following reaction (de Beer, 2008):

$$Mt + wCl_2 + xHCl \rightarrow H_yMtCl_zMt \qquad [1]$$

Where Mt denotes Pt, Pd, Rh, Ru, Ir and Au; and w, x, y and z are respective stochiometric coefficients. Equations 2 and 3 are the reactions that occur in the formation and thermal decomposition of $(NH_4)_2PtCl_3$ to recover platinum. Equations 4 and 5 are the reactions that occur in

the formation and the thermal decomposition of $Pd(NH_3)_2Cl_2$ to recover palladium.

$$H_2PtCl_6 + 2NH_4Cl \rightarrow (NH_4)_2PtCl_6 + 2HCl \quad [2]$$

$$(NH_4)_2PtCl_6 + \Delta \rightarrow Pt + 2NH_4Cl + 2Cl_2 \quad [3]$$

$$PdCl_2 + 2NH_3 \rightarrow Pd(NH_3)_2Cl_2 \quad [4]$$

$$Pd(NH_3)_2Cl_2 + \Delta \rightarrow Pd + 2NH_3 + Cl_2 \quad [5]$$

Gold, Rhodium and Iridium are recovered by Ion-Exchange using organic and inorganic resins which are continuously regenerated in a closed loop; while non recovered base metals are recovered through precipitation by raising the pH using caustic soda (NaOH) to a pH range of 11 to 12 (de Beer, 2008; Rademan, 1995) to improve the purity of PGMs. From the above equations, NH_4Cl, NH_3, HCl and H_2SO_4 are the expected contaminants in the brine since they are in excess when the reactions occur. The other contaminant that is expected is NaOH. The brine is also expected to have a pH range of 11 to 12.

The other source of wastewater is rainwater runoff from road drains within the BMR and PMR plants. Rainwater runoff generally contains oils, organics, solid materials and other matter that the running rainwater picks up in the drainage system. Figure 2 illustrates the simplified PMR and BMR process water circuits. The wastewater is stored in the effluent pond before it is treated using evaporative crystallisation to recover water and a complex mixed salt. Overall, a typical BMR and PMR process recycles approximately 35% of the process feed water.

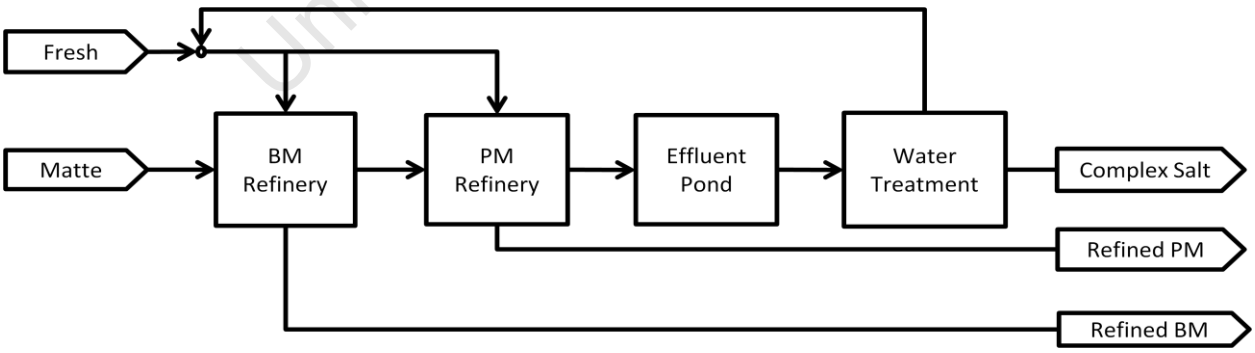

Figure 2: A typical block flow diagram of PMR and BMR process water circuit

2.1.3 Gasification brine

The Sasol plants located in Secunda and Sasolburg produce approximately 41% of South Africa's liquid fuel through gasification of bituminous low-grade coal into synthesis gas, which is a starting material for the Fischer-Tropsch process (van Dyk and co-workers, 2006; Mahlaba, 2006). The process uses large volumes of water in its operation for a wide range of process applications, such as steam generation and process cooling. The process produces a large volume of inorganic wastewater, which contains various dissolved and undissolved salts through demineralization, desalination, softening, ion exchange, evaporative processes (Mooketsi et al., 2007) and so forth.

2.1.4 Gasification brine contaminants

Figure 3 illustrates the Sasol inorganic hypersaline brine formation chain. According to Mahlaba (2006) different applications of water in the synfuels complex generate highly concentrated inorganic hypersaline brines, and the total brines accumulating in the complex contain a combination of used chemicals, raw water, mine water and salts originating from coal and ash. The brines enter the synfuels complex at approximately 250 ton/day, and end-up in water that circulates the complex (Mahlaba, 2006).The evaporative crystallizer unit, the solar pond and the Ash system recover 20, 35 and 45% of the salts from the Snyfuels Complex product stream respectively. The current method of storing the produced salts is disposing them into the ash system and solar ponds (Mahlaba, 2006; Kwaket al., 2005).

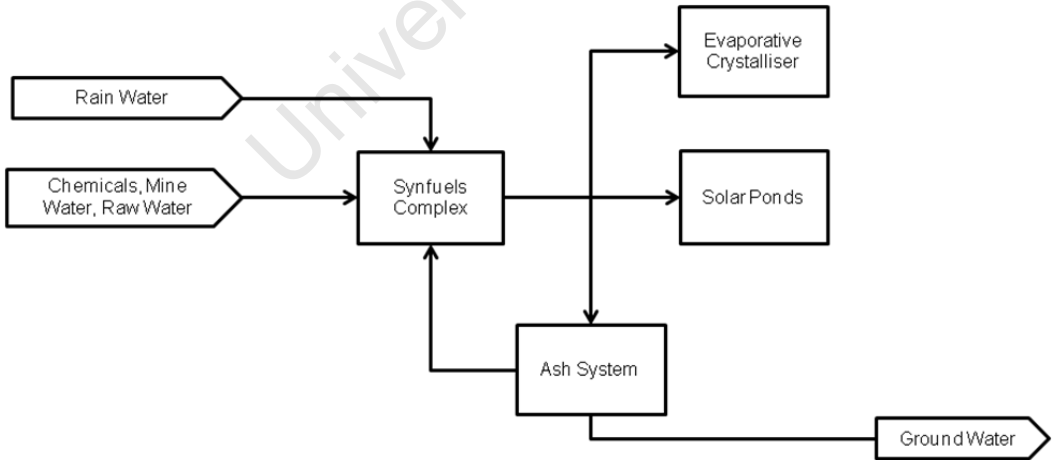

Figure 3: The SASOL inorganic hypersaline brine chain (Mahlaba, 2006)

Table 1 presents the typical Sasol hypersaline brine concentration. The brine has a high Na, Cl and SO_4content in the 1000 ppm (mg/L) range. Typical saline brines at Sasol Synfuels contain: Na (2% - 4.4%), Cl (5%), Ca (0.12%), K (0.38%), Mg (0.059%) ions and trace elements such as Fe, Mn, Cr, V, Ti, P, Si and Al (Mooketsi et al., 2007).

Table 1: The typical Sasol wastewater concentration (Mooketsi et al., 2007)

Parameter	Units	Brine
TDS	g/L	4.40
Na	g/L	0.96
Cl	g/L	2.22

2.2 Brine characterisation

The characterisation of aqueous electrolyte systems is increasingly gaining importance due to its important role in a wide range of processes, which include crystallisation, seawater desalination, corrosion, hydrometallurgy and environmental pollution studies (Kakhu and Pantelides, 2003). There are three main principle steps in brine characterization, namely brine sampling, brine analysis and modelling (APHA, AWWA & WEF, 1998). Each of these principle steps is dependent on the other. Modelling is dependent on the accuracy of the brine analysis, which in turn is dependent on the sampling techniques used in brine sampling.

2.2.1 Sampling

The fundamental aim of sampling is to obtain samples that represent the element of interest (APHA, AWWA & WEF, 1998). The key factors to consider when conducting brine sampling are the sampling and handling techniques.

According to Pulles et al. (1996), Pulles (1993), APHA, AWWA & WEF (1998), Gardner and co-workers (1993) and Water the following factors are important when planning and conducting a sampling program:

- The use of sample labels in order to avoid sample misidentification;
- The use of appropriate sample containers;
- The selection of a suitable number of samples and sample volume because a single sample is

insufficient to reach a reasonable desired level of confidence;

- The use of appropriate sample seals to avoid sample contamination;
- The recording of all relevant information in a bound logbook;
- The storing of samples for a recommended time limit before analysis

Well-executed preservation techniques prevent chemical changes that inevitably continue after sample collection. Where changes in basic water qualities occur quickly, temperature, pH, conductivity, turbidity and alkalinity should be determined immediately after sample collection (Pulles et al., 1996; Pulles, 1993). Microbiological activity may affect the nitrate-nitrite-ammonia content, phenol, or reduction of sulphate to sulphide (U.S.EPA, 1986). The shorter the time lapsed between sample collection and analysis, the more accurate the analysis results (Water Pollution Control Federation, 1986; U.S.EPA, 1986; U.S.EPA, 1982).The Water Pollution Control Federation (1986)suggests that, in order to minimize the potential for volatilization or biodegradation of samples, it is good practice to keep the samples as cool as possible without freezing them, preferably at 4°C. Samples should be analysed as soon as they arrive in the laboratories. No single method of preservation is adequate; therefore samples should be preserved according to the desired parameter determination.

Preservation methods are somewhat limited and they serve the purpose of delaying biological action, hydrolysis of chemical compounds and complexes, and reduction of volatility of water components. Preservation methods are limited to the control of pH, chemical addition as a digestion mechanism, the type of container material used, refrigeration, filtration and freezing (APHA, AWWA & WEF, 1998).

Table 2 presents a brief summary of the recommended sample containers, preservation conditions and the holding time limit when conducting various sample analyses. These recommendations serve as guidelines and should be carefully considered when planning a water characterisation program.

Table 2: Sample preservation (Pulles, 1993)

Determination	Sample container	Recommended preservation conditions	Maximum holding period
pH	Pyrex	Analysis on-site preferably	24 hours
Hardness, M alk., Cl, Acidity, SO_4, colour, SS, dry solids	Plastic or Pyrex	Refrigeration at 4°C	48 hours
Tasting, threshold odour	Pyrex	Refrigeration at 4°C	Less than 24 hours
Dissolved oxygen	-	Determine on-site	No holding
PO_4	Plastic	40 mg/l $HgCl_2$, refrigeration at 4°C and darkness	24 hours
CN^-	Pyrex	2 ml NaOH, pH 10, Refrigeration at 4°C and darkness	24 hours
Al, B	Plastic	5 ml HNO_3	4 weeks
Heavy metals, total	Plastic	5 ml HNO_3	4 weeks
Metals, dissolved	Plastic	Filter: 3 ml/l of 1:1 /HNO_3	4 weeks
TOC (Total organic carbon)	Pyrex	2 ml H_2SO_4, pH 2, 4°C	1 week
Hydrocarbons	Pyrex	2 ml H_2SO_4, pH 2, 4°C	24 hours
Phenols	Pyrex	1.5 ml H_2PO_4 and 10 ml 10% $CuSO_4$ solution	1 week
Bacteriology	Sterile plastic bottles/ bags	Sterile flasks with thiosulphate, Refrigeration at 4°C vital	24 hours
Nitrogen, Ammonia	Plastic or Pyrex	40 mg/l $HgCl_2$, refrigeration at 4°C	1 week
Nitrogen, Kjeldahl	Plastic or Pyrex	40 mg/l $HgCl_2$, refrigeration at 4°C	Unstable
Nitrogen, Nitrate	Plastic or Pyrex	40 mg/l $HgCl_2$, refrigeration at 4°C	1 week
Sulphide	Plastic or Pyrex	2 ml/l Zn acetate	1 week
Conductivity, Fluoride	Plastic	Non required	-
Oil and grease	Plastic	2 ml/l H_2SO_4 at 4°C	24 hours
Mercury	Glass	-	4 weeks

2.2.2 Water analysis

Figure 4 illustrates a schematic summary of water analysis techniques used to determine frequently encountered parameters in industrial brines and various other water systems. It is broken down into two categories, namely the general analysis and the major and trace elements analysis. The major and trace elements analysis category is broken down into four categories, namely anion and cation analysis, ammonia and phosphate analysis, trace metals analysis and other analysis.

The general parameters are pH, conductivity, chemical oxygen demand (Smith, 1978a), density and total organic carbon (APHA, AWWA & WEF, 1998).The major cations that are encountered in many industrial water systems are sodium, potassium, calcium and magnesium, whereas the major anions are chloride, sulphate, fluoride and carbonate (alkalinity) (Smith, 1978b). However, the anions and cations depend on the industrial process chemistry. The different forms of nitrogen are organic and inorganic nitrogen the sum of which is equal to the Total Kjeldahl Nitrogen (TKN) (Smith, 1979a).

Trace metals analysis is the determination of metals in trace quantity in water matrices. The brine trace metals content is chemical process dependent. For example, the metallurgical brine would contain trace amounts of platinum group metals, whereas the gasification brine would likely not contain any platinum group metals. Figure 4 also presents a list of the general trace elements encountered in many industrial brines as summarised by (1998; Smith, 1979b).

The "Other" analyses include the determination of boron, silicon, cyanide, phenol and other hydrocarbons, sulphide, biochemical oxygen demand and turbidity (APHA, AWWA & WEF, 1998; Smith, 1980). These determinations are highly process dependent and often require specialised equipment in their respective analyses.

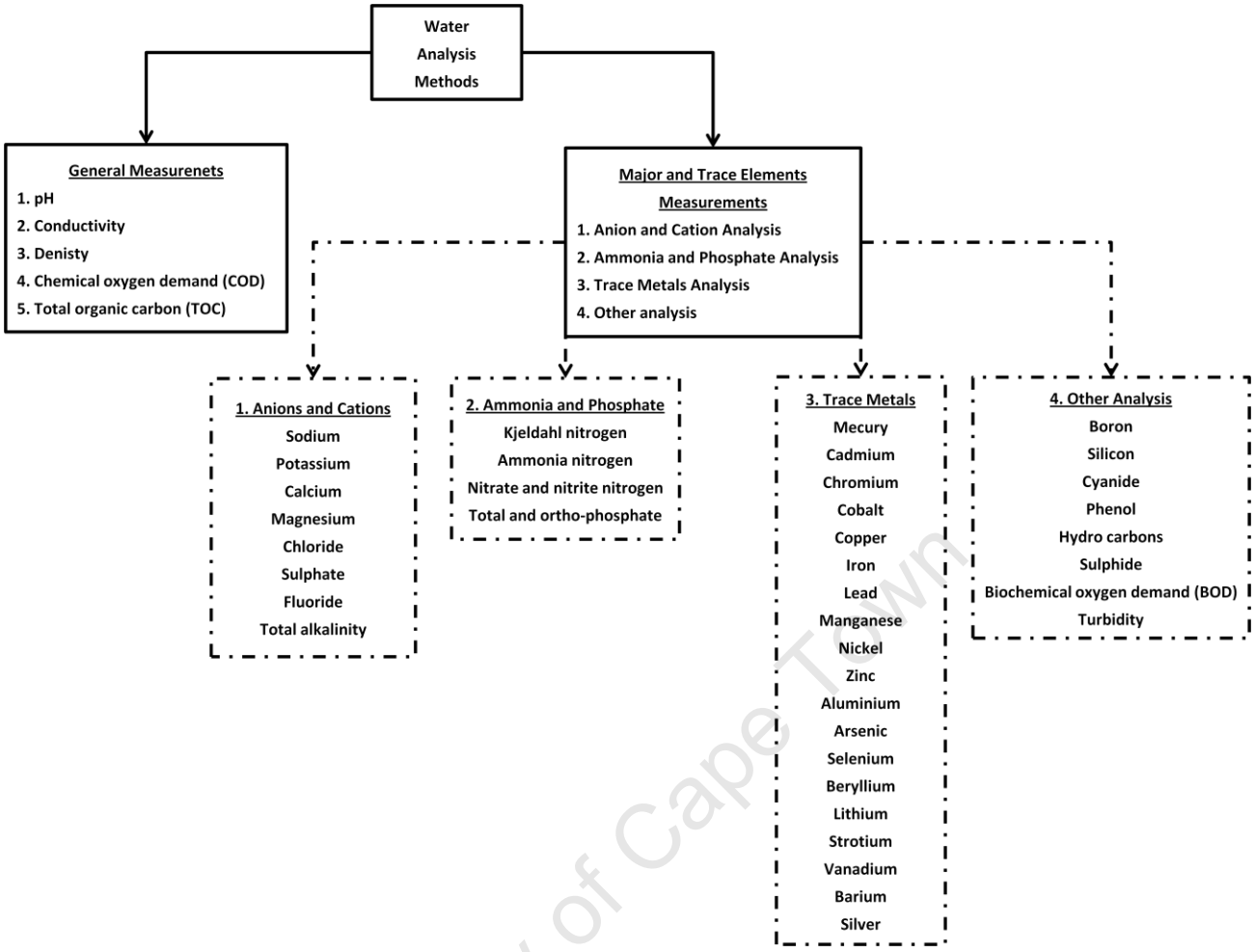

Figure 4: A summary of water analysis methods of major parameters (Smith, 1978b; Smith, 1979a; Smith, 1979b; Smith, 1980)

2.2.3 Analytical technique selection

According to EPA (1999), when choosing suitable analytical methods for analyzing water solution, it is vital to consider the following technical and economic criteria:

- The sensitivity of the method: The analytical technique must be adequately sensitive to measure the presence and concentration of the water contaminant of interest;
- The reliability (or bias and precision) of the analytical results: An analytical method is reliable if it consistently produces similar results when similar samples are analyzed over a set period. Bias and precision are two principle measures of reliability. Precision is the level of results reproducibility between repeated measurements of a specified parameter in identical samples;
- The specificity or selectivity of the technique in the presence of interferences: This is the

ability of the method to determine the component of interest in the presence of other contaminants and interferences;

- The availability of the equipment, facilities and trained personnel required to conduct the analysis;
- The rapidity of analysis to permit routine use;
- The costs of the analysis

The above criteria are important as they provide a strategic approach to conducting sample analysis.

2.2.4 Ion imbalance

Ion imbalance is the relative measure between anions and cations in an aqueous solution. Ion imbalance is frequently encountered in water characterisation (Murray and Wade, 1996). The ion balance is a fundamental measure of data quality of chemical analysis based on the electroneutrality of ionic solutions in precipitation and crystallization aqueous chemistry (Noguchi and Hiroshi, 2004). The ion balance is generally characterized by the balanced ionic concentrations of the following nine major ions: H^+ and OH^-(pH), SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+} and K^+ (Murray and Wade, 1996; Noguchi and Hiroshi, 2004). However ion imbalance is not limited to the above species which fundamentally depend on the water system process and chemistry. Ion imbalance in water analysis is a major problem as it results in inaccurate thermodynamic modelling. In order to minimize ion imbalance, it is essential to understand its main causes.

There is significant amount of work conducted on ion imbalance in natural aqueous solutions and municipal wastewater for which literature is available since these water systems prevail at low concentrations and neutral pH. There is, however, scarce amount of literature on ion imbalance associated with industrial brines due to the complex nature of industrial brines which are wholly process dependent.

2.2.4.1 Causes of ion imbalance

In their work, Noguchi and Hiroshi (2004) measured HCO_3^- (bicarbonate) after having measured other common major ions in river water with the aim of minimising ion imbalance. They found that the unaccounted HCO_3^- was indeed the cause of the imbalance. The type of ion chromatography equipment they used could not measure carbonate concentration, they thus determined the carbonate

content using another method. They approximated the HCO_3^- concentration on the basis of the equilibrium between atmospheric CO_2 and dissolved HCO_3^- using the following expression:

$$[HCO_3^-](\mu mols/L) = 1.24 \times 10^{(pH-5.35)}$$

They found that upon accounting for the carbonate concentration, there was a very significant decrease in ionic imbalance.

Lahav et al. (2002) showed in their calculations and data on rivers, lakes, and reservoir water systems that these water systems can be up to 30 times oversaturated with CO_2, while ground-water systems can be up to 100 times oversaturated with CO_2. This thus resulted in high carbonate content in the water systems.

In their work Murray and Wade (1996) found that pH and species concentration affect water analysis results. They found that extremely low and high pH samples had as much as 100% resultant concentration error associated with them as illustrated in Figure 5. They also found that the presence of unaccounted titratable components, such as organic acids, potentially result in significant ion imbalances. The high H^+ or OH^- content in low or high pH samples, the protonation of ligands and the hydrolysis of metals have a significant influence on the ion balance check as illustrated in Figure 6. In addition to that, the complex formation between protonated ligands and metal cations and between hydrolysed metal cations and strongly binding ligands have a significant influence on the ion balance check. These findings were obtained using simple water systems. The effects would thus be more significant when considering the complex multi-component industrial brine systems.

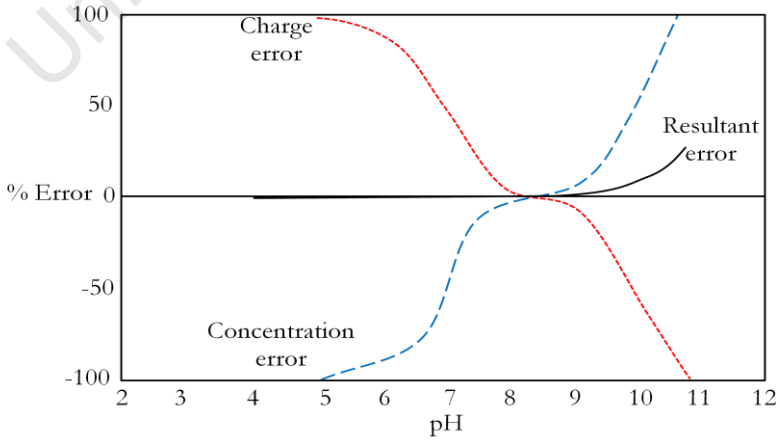

Figure 5: Error as function of pH (Murray and Wade, 1996)

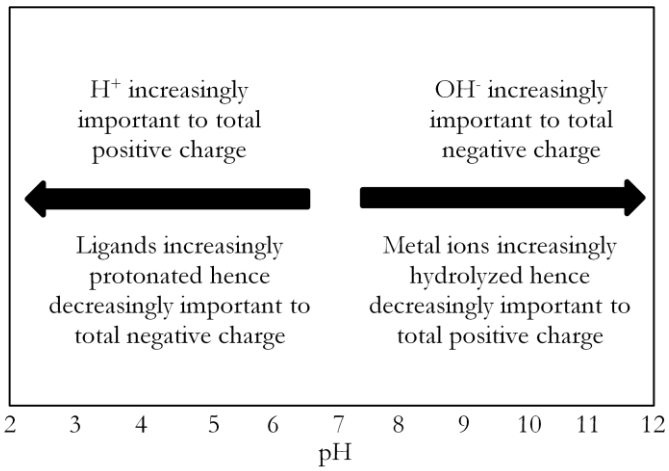

Figure 6: General trends found when calculating anion-cation imbalance (Murray and Wade, 1996)

It is evident that ion imbalance should be expected in the analyses of complex brines. Numerous available thermodynamic tools and software predict the interactions of ions in solution that contribute to the ion imbalance. Murray and Wade (1996) recommend that such thermodynamic modelling tools be utilised if accuracy is to be achieved in an ion balance check.

2.3 Eutectic Freeze Crystallization

2.3.1 Crystallisation

Crystallization is a first order phase transition, a transition point at which solid and liquid are in equilibrium. Crystallization occurs in super saturated systems created by change in concentration, temperature or pressure. The latter parameters influence the driving force required to overcome the nucleation barrier due to interfacial tension (Bermingham et al., 2001). In this process there is a great tendency of large crystals forming due to the crystal growth associated with crystallization. Secondary nucleation is likely to occur in crystallization processes due to low supersaturation, and due to low order kinetics, the process is very slow. Secondary nucleation is the formation of nuclei attributable to the influence of existing microscopic crystals in an aqueous solution (McCabe et al., 2001).

2.3.2 EFC

In eutectic freeze crystallization (EFC), supersaturation is controlled by depressing the system temperature in order for the system to move from undersaturation to supersaturation. Figure 7 illustrates a typical water-salt binary system phase diagram. The cooling of an undersaturated solution with a composition and temperature at point A results in a decrease in system temperature until the ice

line is reached at point B. At this point the first ice crystal forms in the liquid solution, and further cooling results in a decrease in water composition in the bulk solution and a concentrated liquid solution, causing the system to move from point B to point C. With further cooling, more ice forms and the system remains on the ice line and moves from point C to point D, the eutectic point. At the eutectic point there exists the simultaneous formation of pure ice and pure salt. The separation is achieved gravitationally due the difference in ice, salt and mother liquor densities as illustrated in Figure 8. EFC thus utilizes the above principle to obtain highly pure water, in the form of ice, and salt from a liquid solution.

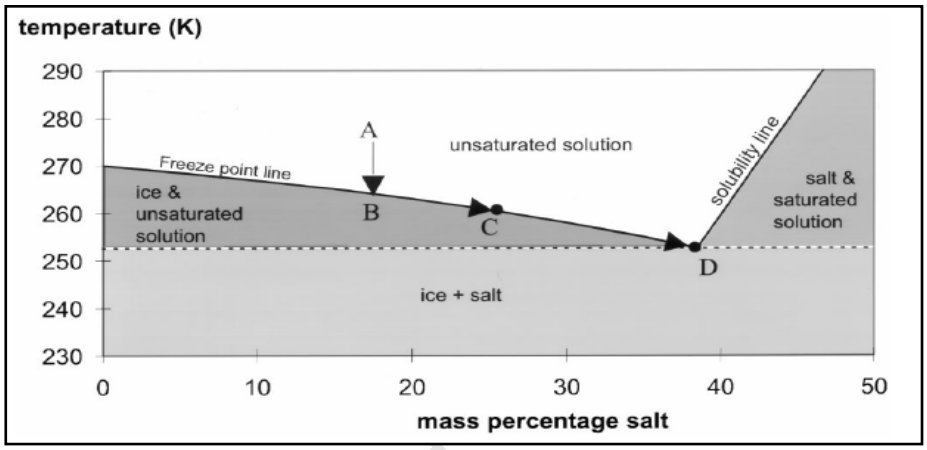

Figure 7: Typical phase diagram for an inorganic aqueous binary system

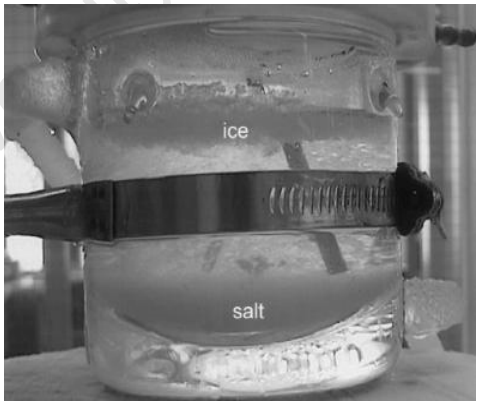

Figure 8: An EFC set-up operating at eutectic conditions, (van der Ham et al., 1998)

EFC is the simultaneous crystallization method used to separate salt and ice crystals at eutectic conditions. The high-density difference between ice and salt makes it possible to conduct EFC and the separation of the solid phases in one reactor is achieved using gravity as mentioned earlier.

EFC produces crystals with very high purities and saves up to 70% energy compared to conventional evaporative crystallization techniques. The main cause for the lower energy consumption is the fact that the latent heat of crystallization for water is a factor of 6.8 lower than the latent heat of evaporation (Pronk et al., 2008); however, the relatively higher investment costs and scale formation are the most prominent disadvantages of EFC.

Figure 9 illustrates the continuous EFC process proposed by van der Ham et al. (1998). The process has four main operating steps, namely: the crystallization of salt and ice; the separation of the resultant salt and ice; washing of the ice; and the filtration of the salt. They proposed that a continuous process is best in order to avoid sub-cooling, to aid control and to operate economically.

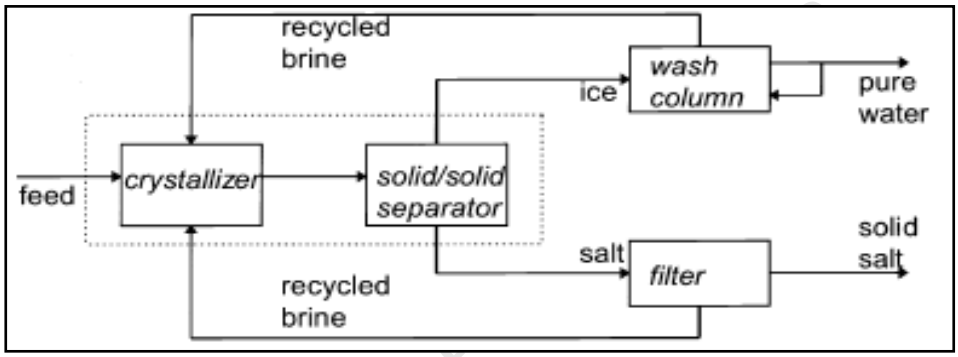

Figure 9: Schematic representation of the EFC process for the production of pure water and salt from waste or process streams (van der Ham et al., 1998)**.**

2.3.3 Multi-component systems

The brines under consideration are multi-component systems hence the separation of the salts in the brine has to be conducted such that the salts are sequentially crystallized out of the solution in the order of their decreasing eutectic temperatures. A multi-component system will have complex phase diagrams but the eutectic conditions can still be determined for these systems using thermodynamic simulation. Thus, phase diagrams for the brine systems would enable one to determine the operating temperature and theoretical yields of ice and salt (Stepakoff et al., 1974). The development of these phase diagrams depends on accurate water analysis results.

Work done by Barduhn and Manudhane (1979) on the investigation of eutectic temperatures of natural synthetic waters with aqueous mixtures comprising various ions, namely Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, $SO4^{2-}$ and HCO^{3-}, showed that the EFC process is feasible and economically viable when operated

at temperatures higher than -25°C. When operating at a temperature range below -25°C, the energy costs rise steeply with further decrease in temperature due to the larger energy required to operate at extremely low temperature. However, when operating at temperatures at or above this range, the process is economically viable. Therefore, the economics of employing EFC strongly depend on the operating temperature that is required to completely separate salt from water. It is thus important to quantify all the contaminants in the brine when conducting the analysis.

In order to estimate the eutectic operating conditions of multi-component systems, phase diagrams are developed using thermodynamic modelling based on the water system species analyses results as input data. Ternary and quaternary phase diagrams are generated and provide information on eutectic temperature and composition of a variety the brine systems. In some cases, brine systems are contaminated with salts that have almost similar eutectic temperatures. Figure 10 illustrates the eutectic temperature and composition of several binary aqueous electrolyte solutions. Suppose a brine system is dominantly contaminated with Na_2SO_4 and $MgSO_4$, the eutectic temperatures of these salts are -3.6 and -3.9, respectively. Seeding is applied to induce crystallisation of a specific solid in a supersaturated aqueous solution thus aiding crystal growth of that specific solid. In this case, Na_2SO_4 seeds would be used to induce Na_2SO_4 salt crystallisation while $MgSO_4$ and ice crystal seeds would be used to induce $MgSO_4$ salt and ice crystallisation respectively, aiding the crystal growth of these specific solids. Seeding thus results in the recovery of salts and water of high purity. The cost of cooling depends on the operating temperatures. The lower the multi-component brine system's eutectic temperature, the higher the cost of cooling (van der Ham, 1999). The cooling crystallizer is designed based on the desired crystal size distribution which is a function of residence time and crystallizer volume (a function of solids density) (Vaessen, 2003). All in all, the recovery of highly pure salts and ice, the prediction of the eutectic temperature and composition, the evaluation of the economics of EFC and the design and optimisation and operation of the EFC crystallizer and process equipment are all fundamentally dependent on accurate brine analysis.

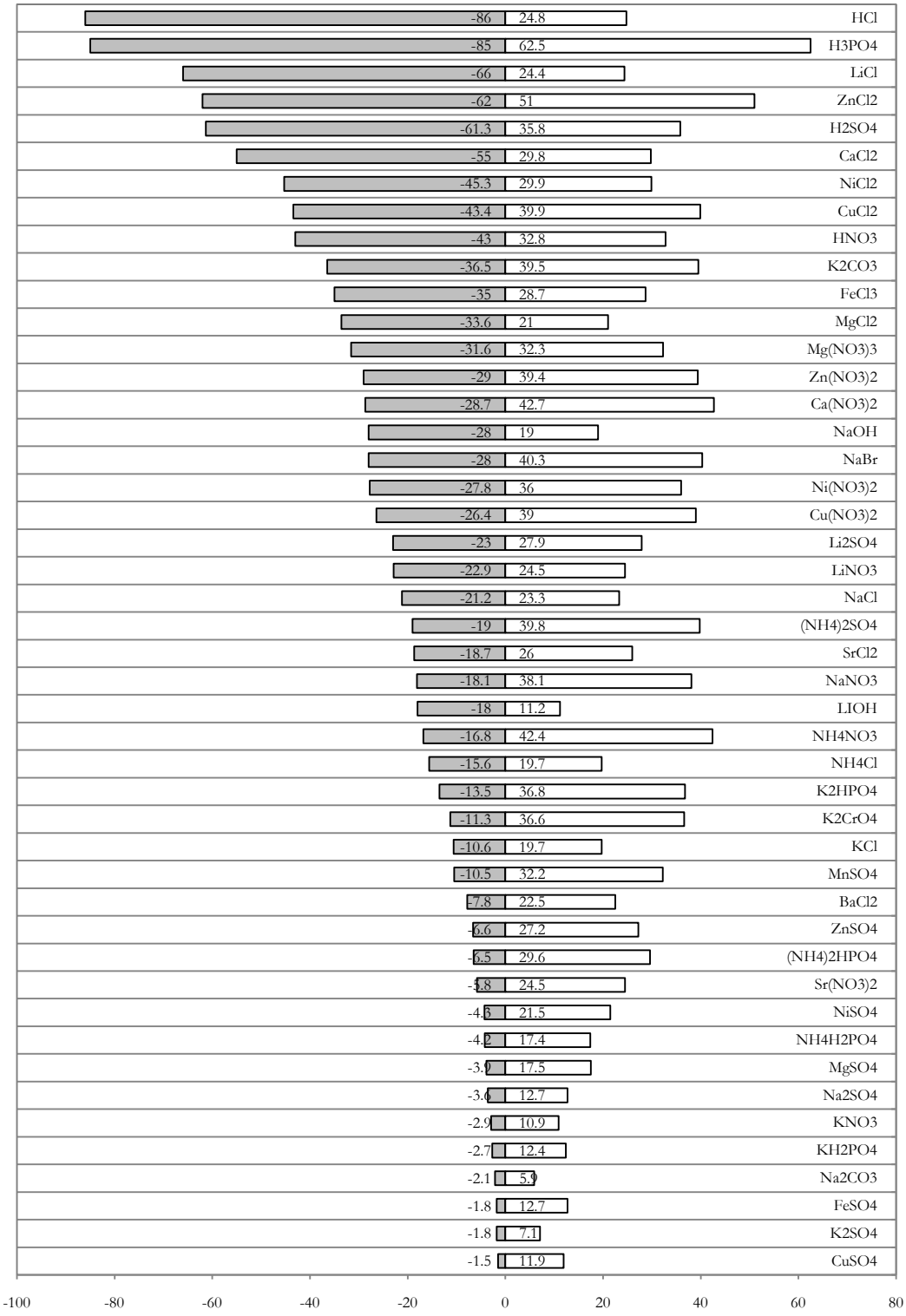

Figure 10: Eutectic temperature [°C] (left) and composition [wt.%] (right) of several binary aqueous electrolyte solutions (Vaessen, 2003)

2.4 Relevant theory

2.4.1 Electrolyte chemistry

By definition, an electrolyte is a substance that contains free ions and acts as an electrically conductive medium, mostly when in a solution (Harned, 1968). Electrolyte solutions are principally formed when a solute (salt) dissociates (or ionises) into ions in a solvent (usually water) due to the thermodynamic interactions between the solvent and the solute molecules, in a process called dissociation (or ionisation) (Petrucci, 1971). The dissociation of salts in water results in the separation of cations (positively charged ions) and anions (negatively charged ions). For example, KCl (solute) dissociates in water (solvent), to form K^+ (cation) and Cl^- (anion) according to the following dissociation reaction:

$$KCl_{(s)} \rightarrow K^+_{(aq)} + Cl^-_{(aq)} \quad [6]$$

Under suitable conditions, gases dissolve in solvents to form ions in solution (Sandler, 1999). For example, carbon dioxide gas dissolves in water resulting in a solution that contains hydronium (H^+), carbonate (CO_3^{2-}), and bicarbonate ions (HCO_3^-). Concentrated electrolyte solutions are solutions with high concentrations of ions, while dilute electrolyte solutions are solutions with low concentrations of ions.

Aqueous electrolyte solutions exist in many industrial processes such as water treatment, seawater desalination, distillation and biological processes (Meyers and Sandler, 2002; Sandler, 1999).

2.4.2 Alkalinity and acidity

Alkalinity is the acid neutralising capability of a water system and is equivalent to the amount of standard strong acid that is required to take the water solution to a defined end point. While, Acidity is the base neutralising capacity of a water solution and is equivalent to the amount of standard strong base that is required to take the water solution to a defined end point (Pulles et al., 1996).Acidity is seldom used due to the difficulty of measuring the base required to reach the end point.

In a water matrix, the total alkalinity comprises of the contributions by HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, $H_3SiO_4^-$, HS^-, organic anions and OH^- (Smith, 2000) subsystems. Where bicarbonate and carbonate concentrations greatly exceed the other species, the total alkalinity can be generally expressed by the bicarbonate and/or carbonate alkalinity (Drever, 1997) depending on the pH condition of the water solution. For example, in terrestrial waters the carbonate system is the dominant subsystem in

expressing total alkalinity (Loewenthal et al., 1989). Industrial brine solutions are more complex than natural water systems based on the presence of multi contaminants, which have an effect on alkalinity of the water matrices. pH is controlled by weak acid chemistry involving the weak acid carbonate, phosphate, ammonia, acetate and water subsystems simultaneously present in solution (Loewenthal, 1997).

In their work, Loewenthal et al. (1989) developed an extension of the characterisation method developed by Gran in 1952, whose method was principally applied to determine total alkalinity (H_2CO_3* alkalinity). Their method was fundamentally an extension of the Gran method for determining the total alkalinity in municipal wastewater where the phosphate, ammonia and short-chain fatty acid systems (acetate and propionate) were present (Loewenthal and co-workers, 1989; Loewenthal, 1997). The extended Gran method was used to find the total alkalinity of carbonate, phosphate, ammonia and acetate subsystems. Hence, according to their method, the key subsystems required to calculate total alkalinity of municipal water system were carbonate subsystem, phosphate subsystem, ammonia subsystem and acetic acid subsystem. Loewenthal and co-workers (1989) thus expressed total alkalinity as follows:

$$\text{Total alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } NH_3 + \text{Alk } H_3PO_4 + \text{Alk HAc} + \text{Alk } H_2O \quad [7]$$

Where Alk $H_2CO^*_3$, Alk NH_3, Alk H_3PO_4, Alk Ac and Alk H_2O are carbonate , ammonia, phosphate, acetic acid and water alkalinity respectively with units mol/l.

Carbonate, ammonia and phosphate subsystems are highly common in hydrometallurgy and gasification inorganic brines. Equation 7 is thus applicable to the inorganic industrial hypersaline brines in evaluating total alkalinity. However, the equation does not take into account the contribution of $B(OH)_4^-$, $H_3SiO_4^-$, HS^- and organic anions as suggested by (Smith, 2000). A possible reason for the exclusion of these elements is their low buffering capacities.

2.4.2.1 **Carbonate system**

Dissolved carbon dioxide reacts with water to form carbonic acid (a weak acid) which dissociates into hydrogen and bicarbonate ions with further increase in pH, according to the following reaction:

$$CO_2(l) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \quad [8]$$

Further increase in pH results in the dissociation of bicarbonate ion into hydrogen and carbonate ion

according to the following reaction:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad [9]$$

With increase in pH, HCO_3^- and CO_3^{2-} formation is favoured and equilibrium reactions equations 8 and 9 shift to the right according to Le Chatelier's principle as illustrated in Figure 11. High pH thus creates a driving force for HCO_3^- and CO_3^{2-} formation.

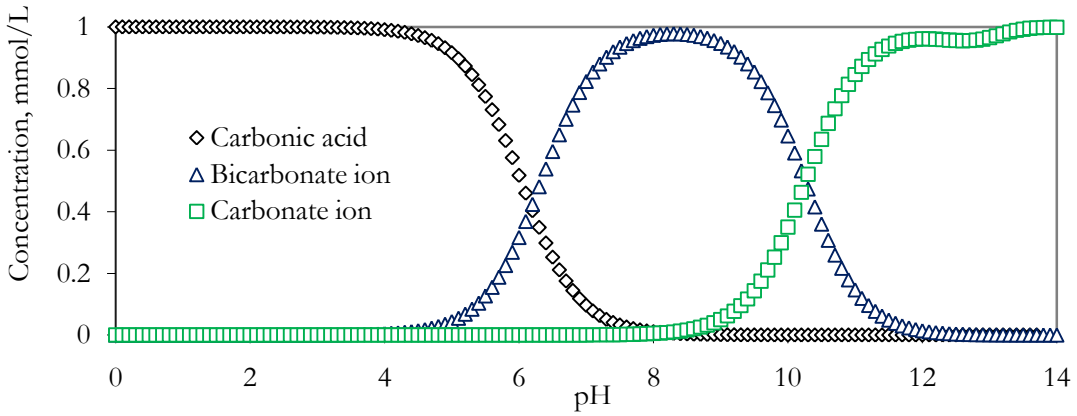

Figure 11: Carbonate speciation diagram (from OLI ™ modelling)

2.4.2.2 Ammonia system

Inorganic nitrogen is predominantly composed of ammonia (NH_3) and ammonium ion (NH_4^+) where nitrate and nitrite (other forms of inorganic nitrogen) are low in concentration. The equilibrium of ammonia in water is represented by the following expression:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + H_3O^- \quad [10]$$

The above equilibrium equation is a function of temperature and ionic strength, and a stronger function of pH. In this case, the ammonium concentration is the difference between FSA and [NH_3]. Based on the Figure 12, it is expected that the ammonium concentration will be approximately zero at pH above 12, but will be significant below pH 11.

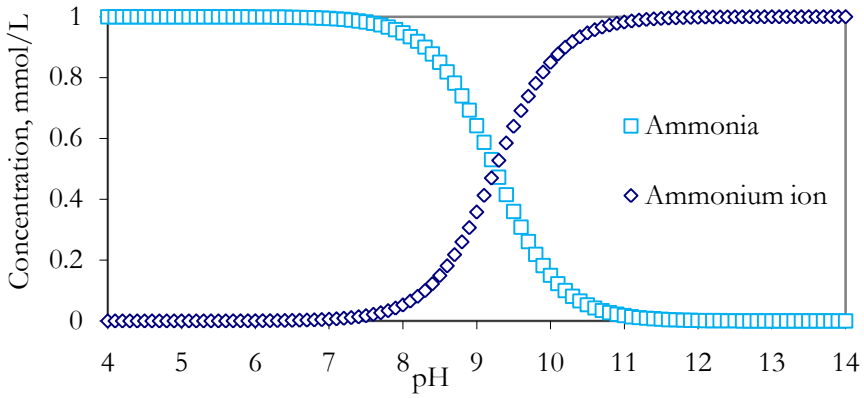

Figure 12: Ammonia speciation diagram as a function of pH (from OLI ™ modelling)

2.4.2.3 **Phosphate system**

Phosphoric acid (H_3PO_4) dissociates in water into hydrogen and $H_2PO_4^-$ according to the following equilibrium reaction:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \quad [11]$$

Further increase in pH results in the dissociation of $H_2PO_4^-$ into hydrogen and HPO_3^{2-} ion, which further dissociates into H^+ and PO_4^{3-} with further pH increase according to the following equilibrium reactions:

$$H_2PO_4^- \leftrightarrow H^+ + HPO_3^{2-} \quad [12]$$

$$HPO_3^{2-} \leftrightarrow H^+ + PO_4^{3-} \quad [13]$$

With increase in pH, HPO_4^- and PO_4^{3-} formation is favoured and equilibrium reactions equations 12 and 13 shift to the right according to Le Chatelier's principle as illustrated in Figure 13. High pH thus creates a driving force for HPO_4^- and PO_4^{3-} formation.

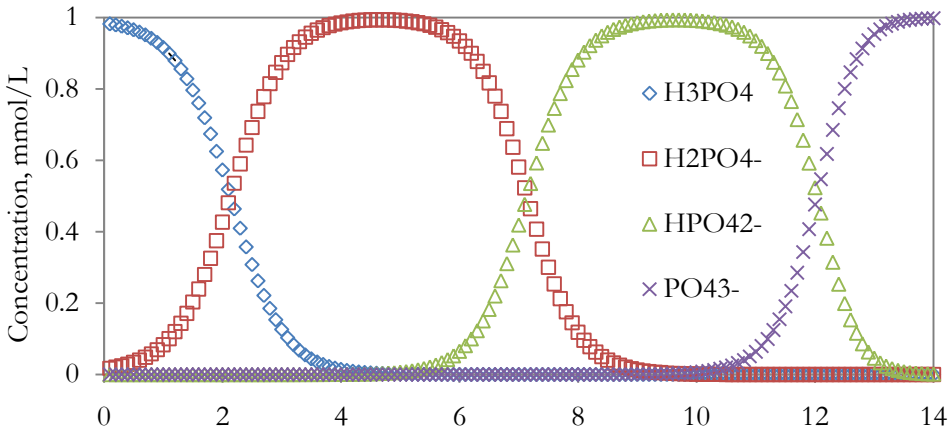

Figure 13: Phosphate speciation diagram as a function of pH (from OLI ™ modelling)

2.4.3 Key characteristics of aqueous electrolyte systems

According to Kakhu and Pantelides (2003), one of the main complexities in modelling aqueous electrolyte systems is determining the complete set of species that are present in these systems. This depends on the accuracy of the water analysis. Even at low electrolyte concentrations, the presence of charged contaminants causes electrolyte systems to significantly deviate from ideality (Thomsen, 2008) and the deviation is even greater in complex multi-component aqueous systems. There are three types of species that can be identified in aqueous systems: (1) undissociated molecular species (e.g. CO_2), (2) ionic species (e.g. Cl^- and Na^+) and (3) solid species (e.g. precipitates and suspended solids) (Kakhu and Pantelides, 2003).

The thermodynamic and phase equilibrium property calculations are essential for the accurate modelling of the wide variety of phenomena that take place in electrolytic systems (Kakhu and Pantelides, 2003). These include the complete ionisation of strong electrolytes, the partial dissociation of weak electrolytes, ionic reactions, complex ion formation, and solid precipitation (Sandler, 1999; Kakhu and Pantelides, 2003). According to Kakhu and Pantelides (2003), the types of computations that can be generally classified are: (1) vapour phase physical properties, (2) equilibrium constants, (3) activity coefficients and (4) property parameters. The use of thermodynamic software that incorporates all these factors in electrolyte calculations is thus essential.

Chapter 3 Brine Characterisation Protocol Development

3.1 Industrial Inorganic Brine Analysis

The parameters to be determined were broken down into analysis components as illustrated in Figure 14. These were based on the summary of all the brine contaminants and parameters presented in Table 3 that were expected in the considered case study brines.

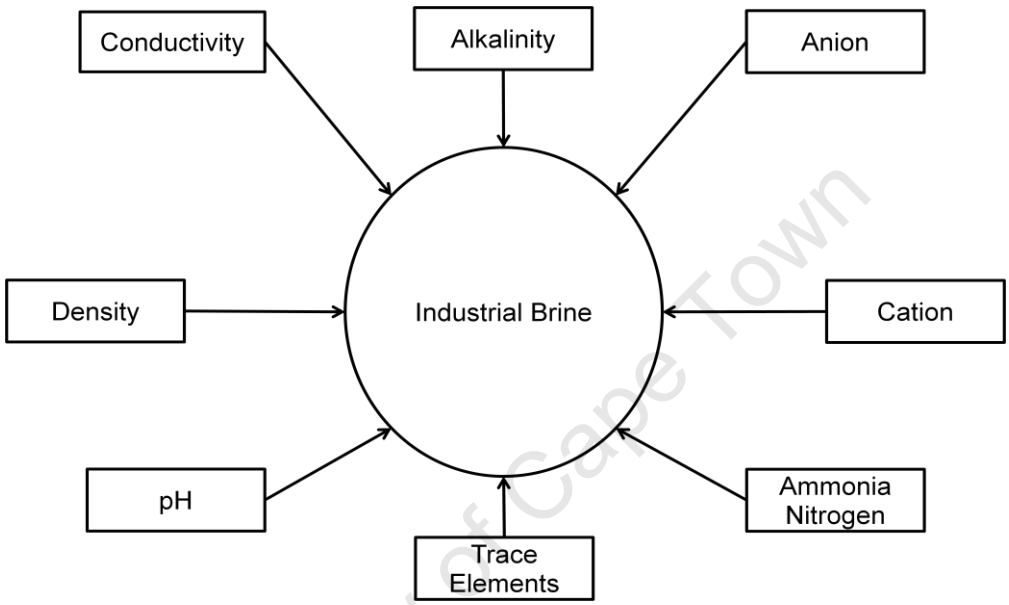

Figure 14: A schematic of a strategy of analysing inorganic industrial brine

The general parameters to be determined were pH, conductivity and density. The anions and cations to determined were Na, Ca, Mg and K cations, and SO_4, Cl anions. The other parameter that were included were total alkalinity (carbonate system), due to its contribution to ion imbalance as seen in the literature review, and the total ammonia-nitrogen (TKN). The trace elements to be determined are summarised in Table 3. This study focused on inorganic brine systems, the analysis of organics was thus not conducted.

Table 3: Revised summary of the case study brine contaminants and general parameters

Major elements	Trace elements	General parameters
Na	Fe	pH
Ca	Mn	Electrical conductivity
Mg	Cr	Density
Na	V	
K	Ti	
SO_4	P	
Cl	Si	
NH_3	Al	
NH_4	Cu	
CO_3	Ni	
HCO_3	Pt	
	Pd	
	Rh	
	Ru	
	Ir	
	Au	

It was important to find analytical techniques that were capable of analysing the parameters in Figure 14 according to the different categories, namely anion, cation, trace element, TKN and alkalinity analysis. However some analytical techniques are designed to simultaneously determine multiple parameters. For example, some ion chromatography techniques are able to determine anions, cations, and ammonium concentrations; some ICP-MS techniques are able to determine N and S which can be indirectly used to determine ammonia-nitrogen and sulphate concentrations respectively. It is thus important to fully understand the type of parameters that the technique is capable of determining.

The analysis techniques were selected based on their suitability for analysing respective parameters. The following subsections outline the suitable equipment and techniques capable of analysing anion, cations and trace elements, ammonia-nitrogen and total alkalinity. The availability of various analytical techniques is presented in Table 4. Some of the methods are readily available, whereas other methods operate on a booking basis.

Table 4: Availability of accessible analysis techniques

Parameter	Method	Availability
Anion	IC	Booking
	Spectro-Quant™	Readily
Cation	ICP-MS/AES	Booking
	AA	Booking
Ammonia-nitrogen	TKN	Booking
	Spectro-Quant™	Readily
Alkalinity	ANATOC analyser	Booking
	Gran titration	Readily

Some methods were not suitable for analyzing the brines and were thus disqualified as presented in Table 5.

- The Spectro-Quant™ method is designed for the analysis of samples with known concentration. It is generally designed for portable and natural water testing as it operates at low concentration ranges. When analysing samples of unknown concentration, the ideal dilution factor is determined by trial and error. The Spectro-Quant™ kit cells are expensive and thus the method of trial and error dilution is not feasible. Each kit is species specific and determines a single parameter at a time. The case study brines are complex water systems containing multiple components.

- The AA method is also parameter specific and determines a single parameter at a time.

- The presence of SO_4 and/or PO_4 causes a reduction in catalyst efficiency of the ANATOC system and thus affects the overall analytical method accuracy. For example, SO_4 and/or PO_4 concentration ≈100ppm can cause a reduction in catalyst efficiency by up to 50% (SEG international Pty Ltd, 2005). Based on the literature review, the case study brines have SO_4content>>1000ppm. Therefore, a greater reduction in catalyst efficiency is expected at these concentration levels.

Table 5: Disqualified parameter analysis techniques

Parameter	Method	Limitation
Anion	Spectro-Quant™	Unknown dilution; Species-specific
Cation	AA	Species-specific
Ammonia-nitrogen	Spectro-Quant™	Unknown dilution; Species-specific
Alkalinity	ANATOC analyser	Malfunctions under presence of PO_4 and SO_4

The chosen methods were thus ion chromatography for anion analysis, inductively coupled plasma mass spectroscopy / inductively coupled plasma atomic emissions spectroscopy (ICP-MS/AES) for cation and trace elements analysis, Total Kjeldahl Nitrogen (TKN) method for organic and inorganic nitrogen analysis and Gran titration method for total alkalinity analysis.

3.1.1 Anion analysis using IC

Compared to conventional electrophoretic techniques, the IC method results in both improved reproducibility and sensitivity (Doury-Berthod et al., 1985). IC is a supreme and uncomplicated method for determining of routine ions in surface, ground, municipal, industrial and potable water systems and requires small samples (Miskaki et al., 2007). ASTM, AOAC, ISO, AWWA, and US EPA regulatory and standard organizations have endorsed the IC method as an effective method for anion analysis. The application of IC for analysis of water systems with parts-per million anion concentration level is widely documented (Smith, 1983). There tends to be interferences caused by substances with retention times coinciding with that of considered anion when working with complex water systems such as sea-water, pore water, industrial brines, concentrated sodium hydroxide and sulphuric acid solutions (Desai et al., 1999). Therefore diluting the water samples theoretically overcomes much of the interference. However, the method is not recommended by many water analysts for analysing F^- in unknown water systems due to poor precision and inconsistent bias associated with the technique.

The Dionex IC measures the concentration of the anions Cl, SO_4, NO_3, PO_4 and Ac. The method relies on the variable adsorption of ions to separate them on an exchange separator column. The peak areas for each ion are calibrated using solutions of known ion concentrations. To inhibit interferences, samples are diluted according to the conductivity of the brines and the dilution factors generally range from 40 to 10 000 factors of dilution. The samples are run for anions on the Dionex HPLC-AS14A exchange column. Dionex API-450 software integrates the area under each conductivity peak, subtracts the background and calculates concentrations of the anions based on calibrations.

3.1.2 Cation and trace elements analysis using ICP-MS/AES

The analysis of micro samples through ICP-MS/AES is a subject that has gained interest over the past decade (Todolí and Mermet, 2006). This is due to its wide range of applications in the analysis of cations and trace elements in water systems from industrial processes, municipal wastewater, terrestrial water systems, and many more. The method has a capability of analysing 90% of the elements in the periodic table in less than a minute to sub ppb level (Jain et al., 1998). The method requires small sample volumes (Kannamkumarath et al., 2002) and is highly efficient and easy to use. It also produces reproducible analysis results in cation and trace elements analysis.

ICP-MS/AES is run by ionising the sample in argon plasma at high temperature and splitting the ions by mass as a measurement basis (Pulles et al., 1996). Filtered samples are diluted to acceptable salinities with 2% HNO_3 as a means of acidifying the samples. Limitations of the technique are generally due to interferences by argon ions produced in the plasma. A well-known interference is between 56Fe and 40Ar16O (Smith, 2000).

The Varian radial ICP-MS/AES measures cations and trace elements concentrations. It has an operating range of mid ppb's to 1000ppm. The equipment measures the concentration of the following elements: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Se, Si, Sr, Ti, V and Zn.

3.1.3 Ammonia-Nitrogen analysis using TKN method

Nitrogen is a nutrient and generally occurs in organic (nitrogen with hydro-carbon attached to it) and inorganic (ammonia, ammonium, nitrate and nitrite nitrogen) forms. Based on the amount of nitrification which occurs in an industrial process, wastewater generally contains either ammonia or nitrate nitrogen. Generally, the nitrite form of nitrogen is not present in large quantities due to its fast oxidation or conversion to nitrate (U.S.EPA, 1986).

The TKN method is an analysis method used to determine both the organic nitrogen and the inorganic nitrogen (free and saline ammonia (FSA) nitrogen) (APHA, AWWA & WEF, 1998). In this case, organic nitrogen is the difference between TKN and FSA, i.e. Organic N = TKN -FSA. This is because wastewater nitrogen is generally present in the organic nitrogen and ammonia forms, with small quantities of the nitrite and nitrate forms (APHA, AWWA & WEF, 1998). However, industrial brines are process dependant and their compositions thus vary according to the chemical reactions in

the process. The equilibrium equation of aqueous ammonia is as follows:

$$NH_3\ (g) + H_2O \leftrightarrow NH_3\ (l) + H_2O) \leftrightarrow NH_4^+ + H_3O^- \quad [14]$$

The above equilibrium equation is a function of temperature and ionic strength, and a very strong function of pH. The ammonia concentration can be obtained from the following expression of $[NH_3]$ as function of pH and FSA (total inorganic ammonia-nitrogen) as developed by Loewenthal et al. (1989):

$$[NH_3] = \frac{FSA \times 10^{-pK_n'}}{10^{-pH_o} + 10^{-pK_n'}} \quad [15]$$

Where pKn' is the apparent ammonia weak acid dissociation constant and has a standard dimensionless value of 9.25 at 25 °C. In this case, the ammonium ion concentration is the difference between FSA and $[NH_3]$. The expression is generic and is thus applicable to all water systems containing ammonia.

TKN is determined as follows:

- The sample is digested to convert the organic nitrogen to ammonia-nitrogen
- The digested sample undergoes a distillation of the total ammonia-nitrogen (organic N and FSA) into an acid absorbing solution
- An acid titration is then conducted to determine the concentration of ammonia

FSA is determined using the same method as TKN but skipping the digestion step.

3.1.4 Alkalinity analysis

The extended Gran method determines the total alkalinity of carbonate, phosphate, ammonia and acetate subsystems by using equation 7. The extended Gran titration method requires knowing values for one parameter for each acid subsystem present. Therefore if total species concentrations for each weak acid subsystem and solution pH are known, then the solution is completely characterised (Loewenthal, 1997). The IC method is used to determine phosphate and acetate concentrations; TKN is used to determine the ammonia concentration; and a calibrated pH probe is used to measure the pH of the aqueous system.

3.2 Thermodynamic modelling

Multiple factors cause difficulties in the modelling of aqueous electrolytic systems based on the following reasons: (1) completely unknown new species can form in water; (2) dissolved inorganic substances ionize to varying degrees; and (3) ionic species tend to precipitate (Stumm and Morgan, 1981). Electrolyte solutions generally deviate extensively from ideality due to the deviation of the activity coefficient from the ideal case value of unity with increasing non-ideality (Pillay, 2004). A comprehensive understanding of the thermodynamic properties of brines is essential and results in better process design, optimization and control (Meyers and Sandler, 2002; Jin and Donahue, 1988). Thermodynamic software is used to conduct thermodynamic modelling on complex aqueous systems. The model can thus be used to characterise the water system by predicting important parameters such as speciation, scaling tendencies, etc…

OLI Stream Analyzer 3.0.10 software is an aqueous electrolyte thermodynamic model that determines aqueous speciation and phase equilibria for multi-component systems. The model uses the Helgeson-Kirkham-Flowers (HKF) equation of state parameters to predict the equilibrium constants. It also uses Bromley-Meissner, Pitzer, Helgeson and Bromley-Zematis equations for activity calculations. The software also has an integrated mixed solvent electrolyte (MSE) database, which is able to achieve modelling temperatures as low as -200°C. The limitations of the software are as follows:

- It does not have a separate activity coefficient model (i.e., it does not have NRTL, Unifac/Uniquac models);
- The non aqueous and vapour fugacity coefficients are characterized from the Enhanced Soave-Redlich-Kwong Equation of State;
- Vapour critical parameters are correlated to find a fugacity coefficient.

The software determines the ion balance and component speciation as a function of temperature and pressure.

Chapter 4 Case Study Brines

Three categories of inorganic industrial hypersaline brines were used as case studies to put the developed industrial brine characterisation protocol into practice. Two different metallurgical brine types and a gasification brine type were sampled from their respective industrial processes. The metallurgical brine consisted of basic (alkali) and mixed brines.

4.1 Methodology

The industrial brine characterisation procedure is illustrated in Figure 15. The principle steps were: brine sampling and transportation; brine storage and preparation; brine analysis which is divided into two categories; namely the general analysis and major and trace elements analysis; and thermodynamic modelling. A component that is not a principle step is the error analysis of the major and trace elements analytical methods.

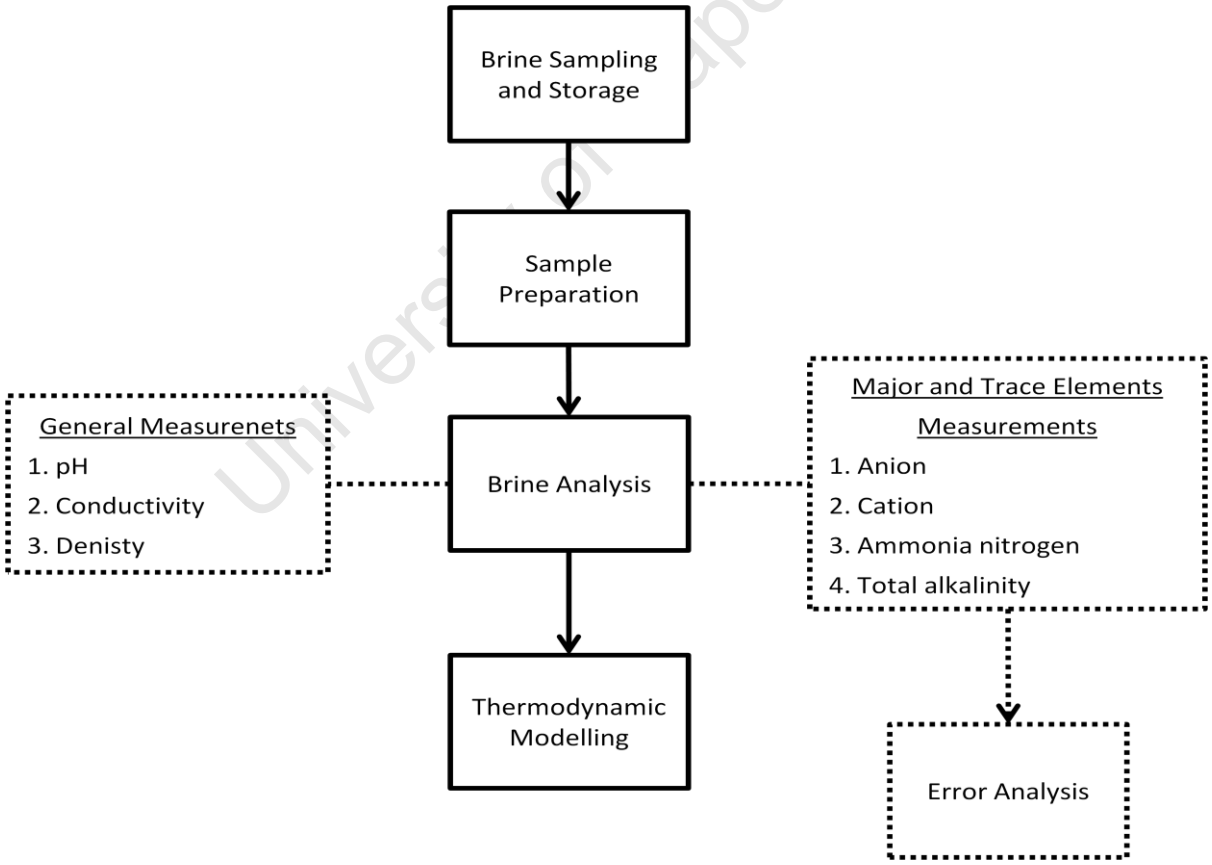

Figure 15: The industrial brine characterisation procedure

4.1.1 Sampling and storage rationale and naming convention

All brine samples were collected into 20 litre plastic labelled containers. The samples were all unfiltered during sampling. No analysis was conducted on site. The brine samples were transported using various modes of transportation to the University of Cape Town (UCT) Crystallisation and Precipitation Unit (CPU) laboratory. Each brine sample arrived at UCT within an average time span of two weeks.

Upon arrival in the CPU lab, the brine samples were filtered through a gravity filter and were stored at room temperature away from the direct sun to limit aqueous chemical reactions. The well-ventilated laboratory maintained an average temperature of 22 ± 2 °C.

Sample labels were derived from the respective industrial processes. The first two letters represented the industrial brine sample type. For the metallurgical brine, the third letter represented the type of metallurgical brine. The letter X followed the first two letters of the gasification brine as it had a single brine type. A summary of the abbreviations of the brine sample types is presented in Table 6.

Table 6: A summary of the abbreviations of the brine sample types

Sample type abbreviation	Sample type
MTB	Basic metallurgical brine
MTM	Mixed metallurgical brine
GSX	Gasification brine

4.1.2 Sample preparation

The brine samples were further filtered through a 0.45 μm cellulose acetate membrane filter during sample preparation to remove microscopic solid particles that would potentially affect sample analysis. All brine samples were collected into 40 and 50 mL plastic bottles, thoroughly rinsed with MilliQ 10MΩ deionised water. All samples were prepared in triplicate for measurement and the determination of standard deviation. The brine samples had different pH, conductivity and concentration characteristics and were thus prepared separately for each analysis method as follows:

- Each case study brine sample sent for anion analysis was diluted to conductivity ≤ 100 μS by the IC operator;

- Each case study brine sample sent for cation analysis was acidified with HNO_3 to maintain

metals in solution. The ICP-MS/EAS operator diluted each industrial brine sample separately to sample concentrations< 100 ppm;

- Each case study brine sample prepared for TKN analysis was diluted by trial and error to a concentration that was suitable for the method to efficiently determine TKN. Each case study brine sample thus had a unique dilution factor;

- Each case study brine sample prepared for Gran titration analysis was diluted by trial and error to a concentration that was suitable for the method to efficiently determine total alkalinity. Each case study brine sample thus had its unique operating dilution factor.

4.2 Brine Analysis

4.2.1 General measurements

The general analyses were conducted in the CPU laboratory as soon as the brine samples arrived. Below is the equipment used to conduct the general analyses.

4.2.1.1 **pH**

Each filtered sample pH was determined using a calibrated Hanna 211 microprocessor pH meter calibrated with pH 4, 7 and/or 10 Merk chemical (Pty) Ltd standard buffer solutions. All industrial brine samples were filtered before measuring the pH measurement. The pH probe was thoroughly rinsed with MilliQ 10 MΩ deionised water before each measurement. The pH meter was calibrated before taking each set of measurements.

4.2.1.2 **Electrical conductivity (EC)**

EC measures the number of ions in solution and is a convenient way of estimating the salinity of a solution (Smith, 2000; Drever, 1997). Each sample EC was determined using the AZ conductivity meter 86505 calibrated with MilliQ 10 MΩ deionised water. The probe was thoroughly rinsed with MilliQ 10 MΩ deionised water before taking each measurement.

4.2.1.3 **Density**

Sample density was determined by obtaining the mass of a known filtered brine sample volume using the calibrated Precisa 205A and 3100C mass scale meter. The ratio of the sample mass and sample

volume was equivalent to the sample density. Distilled water was used as a standard to test the accuracy of the measuring device.

4.2.2 Major ions and trace elements

Each general analysis was conducted upon arriving at the UCT CPU laboratory. The IC and ICP-MS/AES analyses were conducted based on the availability of the machines. '*This was a major limiting factor*'. The TKN analysis was conducted within a week of the arrival of each case study brine sample, with the exception of the coal mining brine, which was analyzed within a month of arrival. The Gran titration method was dependant on the phosphate and ammonia analysis using IC and TKN methods respectively.

4.2.2.1 **Anion analysis**

The Dionex IC was used to determine anion content. In order to reach the detection limit, the samples were diluted using MilliQ 10 MΩ deionised water.

4.2.2.2 **Cation and trace elements analysis**

The Varian radial ICP-MS/AES was used to determine cation and trace elements concentration. In order to reach the detection limit, the samples were diluted using MilliQ 10 MΩ deionised water.

4.2.2.3 **Nitrogen ammonia analysis**

TKN was used to determine both the organic nitrogen and the FSA concentrations. The set-up and the used glassware were thoroughly rinsed before each analysis using MilliQ 10 MΩ deionised water. The reagents used in the method were prepared using MilliQ 10 MΩ deionised water.

4.2.2.4 **Carbonate analysis**

Gran titration was used to conduct the carbonate analysis. Dilutions were conducted using MilliQ 10 MΩ deionised water. The glassware used for the analysis was thoroughly rinsed with MilliQ 10 MΩ deionised water. The reagents used in the method were prepared using MilliQ 10 MΩ deionised water.

4.2.3 Thermodynamic Modelling

Thermodynamic modelling was conducted using OLI Stream Analyzer 3.0.10software. The software

was used to determine and establish ion balances based on the obtained brine analysis results.

4.3 Results and discussion

4.3.1 General chemical parameters

Table 7 presents the obtained general chemical parameter analysis results. The metallurgical mixed brine was the most concentrated case study brine and had the highest EC and density values of 141 mS/cm and 1.15 g/cm^3 respectively. The gasification brine was the least concentrated and had an EC and density of 68 mS/cm and 1.06 g/cm^3 respectively.

Table 7: General parameter analysis results

Component	Units	MTB	MTM	GSX
pH		12.8	9.8	7.0
EC	mS/cm	129	141	68
Density	g/cm^3	1.07	1.15	1.06

4.3.1.1 **Salinity**

An effective means of determining salinity of an aqueous water system is by determining electrical conductivity (EC), which is an indirect measure of the number of ions in solution (Drever, 1997). Therefore, the greater the quantity of dissolved ions in solution, the greater the corresponding conductivity value. Figure 16 illustrates the obtained relationship between total dissolved solids (TDS) and the sample conductivity. In this case, total dissolved solids were defined as the sum of all measured components in each brine sample; namely the sum of cations, anions, total nitrogen and carbonate system. The relationship between EC and the TDS was nonlinear at these high TDS concentrations. The reason for this observation is that as the molar concentration of ions in solutions increases, the conductivity decreases due to electrolytic effects (Eaton and co-workers, 1995; Meris, 2000). Electrolytic effect (kinetic ionic-strength effect) is the general effect that an added electrolyte has on the observed reaction rate constant in solution (McNaught and Wilkinson, 1997).

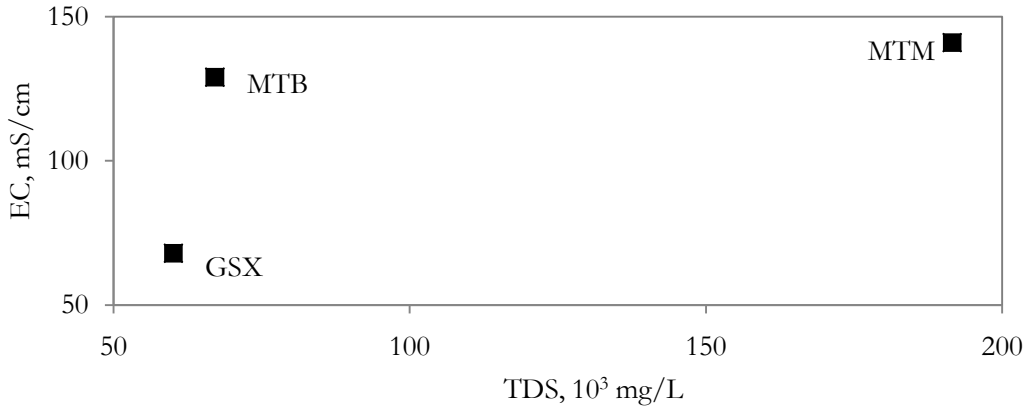

Figure 16: The relationship between EC and TDS

From the results, it was found that the metallurgical brines had relatively higher EC values than the gasification brines. The basic metallurgical brine had an EC value twice that of the gasification even though they had almost equal density values. There were two possible reasons for these observations.

Firstly, the metallurgical brines were relatively high in Na, Cl and SO_4 content. Table 8 presents the limiting conductivity values of general cations and anions in water. Na^+, Cl^- and SO_4^{2-} have conductivity values that are significant and at high concentrations they contribute immensely. Although the gasification brine had Mg and Ca content, which both have higher conductivity values than Na, they were relatively very low in concentration and thus had a smaller contribution towards the EC.

Secondly, the metallurgical brines prevail at extreme low and high pH values relative to the neutral pH gasification brine, thus causing them to have high H^+ and OH^- content. From Table 8, it can be seen that H^+ and OH^- had the highest conductivity values in their respective categories. The presence of these ions thus contributed significantly towards conductivity at extreme brine pH conditions.

Table 8: The limiting ion conductivities in water at 298 K (Perry, 2008)

Cations	Conductivity, mS m^{-1} mol^{-1}	Anions	Conductivity, mS m^{-1} mol^{-1}
H^+	34.96	OH^-	19.91
Na^+	5.01	Cl^-	7.63
K^+	7.35	Br^-	7.84
Mg^{2+}	10.61	SO_4^{2-}	15.96
Ca^{2+}	11.90	NO_3^-	7.14

Figure 17 illustrates the relationship between the TDS and the sample density. The sample density had a more linear relationship with TDS than conductivity had with TDS.

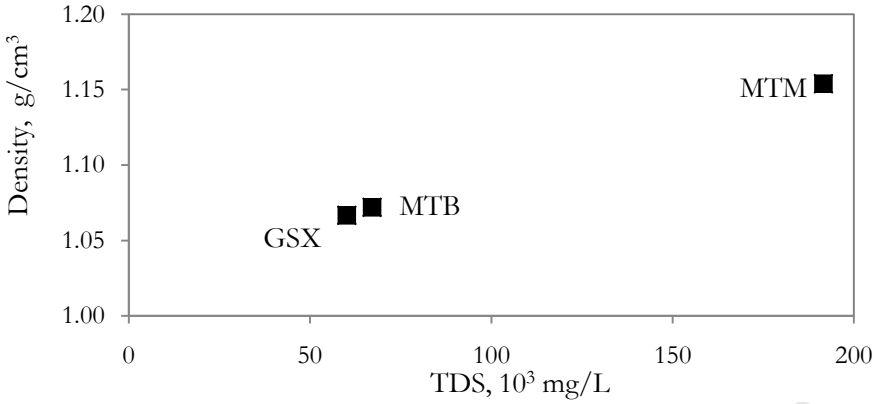

Figure 17: The relationship between density and TDS

4.3.1.2 **pH**

The basic metallurgical brine had the greatest pH value of 12.8. It also had a relatively high Na content. The high pH and Na content were due to the caustic soda (NaOH) used to raise the pH to values between 11 and 12 in the precipitation of non-recovered base metals in the PGM refinery as seen in the literature review.

The mixed brine was a combination of the alkali and acid brines and other wastewater from around the BMR and PMR plants. However, the ratio of the mix was not known and it was thus not possible to conduct a mass balance.

The gasification brine had relatively neutral pH values. The reason being the brine went through a reverse osmosis desalination process. The membranes used in reverse osmosis are very sensitive to pH, and are thus broadly applied in neutral wastewater treatment.

4.3.2 Major and trace elements analysis

Table 9 presents the obtained IC anion analysis results. The IC was generally able to detect PO_4, SO_4, NO_3, NO_2, Cl, and Br in the considered industrial brine samples. All the case study brines were highly concentrated with SO_4 and Cl. The mixed metallurgical brine had the highest Cl and SO_4 content of 37363 and 46963 mg/L respectively. NO_3 concentration was relatively significant and ranged from 785 to 2175 mg/L. PO_4 and Br were detected at somewhat significant concentration levels < 1000 mg/L. NO_2 was only detected in the gasification brine with a concentration of 395 mg/L.

Table 9: Anion analysis results

Component	Units	MTB	MTM	GSX
PO_4	mg/L	450	475	55
SO_4	mg/L	4613	37363	29920
NO_3	mg/L	788	2175	785
NO_2	mg/L	nd	nd	395
Cl	mg/L	13375	46963	11135
Br	mg/L	250	988	85

Table 10 presents the obtained ICP-MS/AES cation and trace elements analysis results. The technique was generally able to detect Na, Mg, Si, K, Ca, Fe, Cd and Ni in the case study brine samples in significant levels. All the case study brines had a high Na content, which ranged between 21149 to 70297 mg/L. The Si and K content were relatively high. The mixed metallurgical brine had the highest Si content of 251 mg/L whereas the gasification brine had the highest K content of 2161 mg/L. The gasification brine also had relatively significant Mg and Ca content of 208 mg/L and 707 mg/L respectively.

Table 10: Cation and trace elements analysis results

Component	Units	MTB	MTM	GSX
Na	mg/L	31353	70297	21149
Mg	mg/L	nd	<1	208
Si	mg/L	94	251	44
K	mg/L	33	110	2,161
Ca	mg/L	4	5	707
Fe	mg/L	<1	<1	nd
Cd	mg/L	1	2	nd
Ni	mg/L	<1	9	1

Table 11 presents the obtained TKN and total alkalinity analysis results. The case study brines had no organic nitrogen content. The basic metallurgical brine had the highest ammonia-nitrogen content of 876 mg/L as NH_3.

The case study brines contained carbonate content. The basic and mixed metallurgical brines had a relatively higher carbonate content of 1652 and 6564 mg/L respectively as carbon. The gasification brine had a carbonate content < 120 mg/L.

Table 11: TKN and total alkalinity results

Component	Units	MTB	MTM	GSX
pH		12.8	9.8	7
Total alkalinity (as carbon)	mg/L	1652	6564	78
CO_3	mg/L	8261	21202	-
HCO_3	mg/L	-	11619	390
TKN (as nitrogen)	mg/L	784	238	25
NH_3	mg/L	876	-	-
NH_4	mg/L	-	18	54

4.3.2.1 **Dominant species contribution**

The most common ion equivalence series of inorganic industrial hypersaline brines is Cl > SO_4 > Alkalinity (HCO_3 and CO_3) for anions and Na > Mg >Ca ≈ K for cations (Hammer, 1986). Na cation, Cl and SO_4 anions were the dominant ions in the case study industrial brine samples. Alkalinity was relatively significant in the basic and mixed metallurgical brine samples.

Figure 18 illustrates the major anion dominance in the case study brines. Cl was dominant in the basic and mixed metallurgical brines. Alkalinity was significant in the basic and mixed metallurgical brines. The total alkalinity in the basic and mixed metallurgical brines contributed 30 and 27 % respectively towards the total anion concentration. Total alkalinity in the basic metallurgical brine contributed more than sulphate towards total anion concentration. The alkalinity contribution in the gasification brine sample of 8 and 1 % was lower relative to the other major anions.

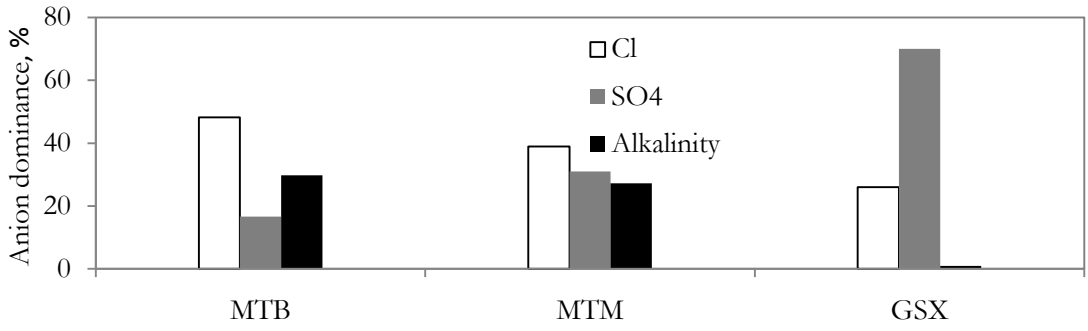

Figure 18: Anion dominance of Cl, SO_4 and alkalinity

Figure 19 illustrates the major cation dominance in the case study brine. Na was the most dominant cation in the case study brines. In the basic and mixed metallurgical brines, ammonium contribution towards total cation concentration was insignificant. Mg and Ca were relatively insignificant in all the case study brines.

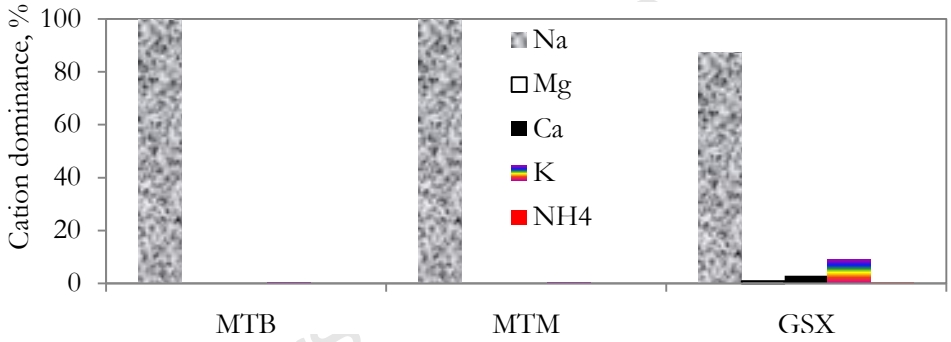

Figure 19: Cation dominance of Na, NH_4, Mg, Ca and K

4.3.2.2 Species chemistry

Sodium

The presence of sodium in the hydrometallurgical brine samples was expected. A major source of sodium ions in the hydrometallurgy brines was the ion exchange process in which Na^+ is used as the exchange ion. In gasification brines, sodium content is also due to other natural sources and treatment chemicals such as NaOCl and Na_2CO_3 (Pulles et al., 1996).

Sulphate

All the case study brines had significant sulphate content. The presence of sulphates in the case study brine samples was expected as found in the literature review. A dominant source of sulphate ions in the hydrometallurgy brine was sulphuric acid used in the leaching process in which metal sulphides are oxidised to metal sulphates in the presence of excess sulphuric acid in the PMR circuit (Khan et al., 2009; de Beer, 2008). A possible reason for sulphate content in these brines was due to pyrite oxidation or its dissolution in water from certain minerals, particularly gypsum (Pulles et al., 1996).

Chloride

All case study brines had significant chloride content, but generally in lower levels than sulphates. The presence of chlorides in the case study brine samples was expected. A dominant source of chloride ions in the hydrometallurgy brine was from excess Cl_2 and HCl used in the dissolution process of PGMs in the PMR circuit. In the PMR circuit there is generally some recovery of the excess chloride, while the rest is discharged into the effluent streams. The presence of chloride in gasification brines is generally associated with sodium ion (Pulles et al., 1996).

Alkalinity

Overall, the total alkalinity consisted of contributions by carbonate, ammonia, phosphate and water subsystems. With the case study brines the carbonate system was the major contributor to total alkalinity by a percentage of 97 – 100 % as illustrated in Figure 20.

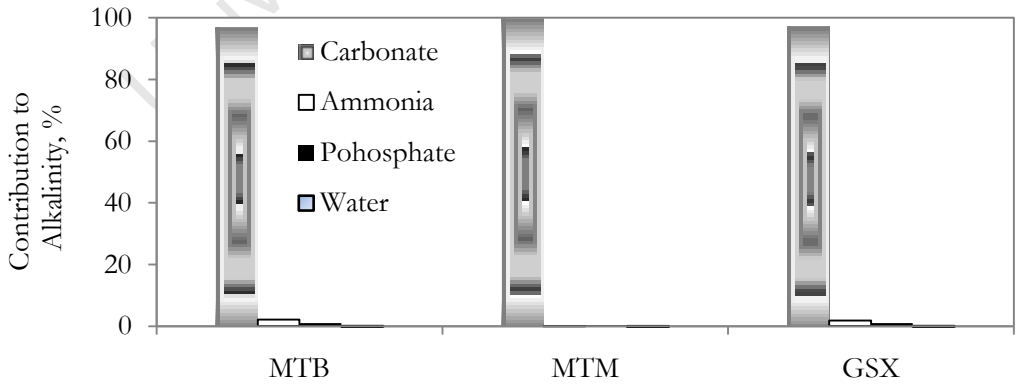

Figure 20: Alkalinity contribution by carbonate, ammonia, phosphate and water systems

pH created an environment that favoured the speciation of the carbonate system along various pH intervals above pH 7. Therefore, the carbonate system was of the form H_2CO_3, HCO_3^- or CO_3^{2-} depending on the brine pH. Dissolved calcium and magnesium ions generally account for the hardness of the water system. In these case study brines, hardness was very insignificant due to the very low Ca and Mg content. Overall, the bicarbonate and carbonate ions gave the case study brines most of their alkalinities.

Ammonia

The presence of ammonia in the metallurgical brine was expected. In the literature review, it was found that excess NH_4Cl and NH_3 are used in the formation and thermal decomposition of $(NH_4)_2PtCl_6$ and $Pd(NH_3)_2Cl_2$ to recover platinum and palladium. The mixed metallurgical brine's low ammonia content was due to one of two possible reasons. Since ammonia is a gas, it could have bubbled off into the atmosphere; or the brine could have gone through an ammonia recovery step removing all ammonia, and thus the ammonia-nitrogen could be the nitrate and/or nitrite forms of inorganic nitrogen. *Remember that TKN is the sum of organic and inorganic nitrogen (ammonia, ammonium, nitrate and nitrite).* Ammonium content in the gasification brines was from the use of ammonium or nitrate based explosives (Pulles et al., 1996; Pulles, 1993) during coal mining operations to recover coal used in the Fischer-Tropsch process. Another contributor was nitrate and nitrite forms of inorganic nitrogen.

Ammonia was in the form of NH_3 in the basic metallurgical brine and NH_4^+ in the mixed metallurgical and gasification brines. This is because in a water system, free saline ammonia (FSA) exists in equilibrium with the ammonium ion, NH_4^+ (Loewenthal, 1997) and the equilibrium is a strong function of pH. FSA is dominant at pH > 9.2, while NH_4^+ is dominant at pH < 9.2. The form of ammonia thus depends on the pH of the brine system.

4.3.3 Error analysis

There are various errors that affect the overall sample analysis results. The most common are reagents error, general method error, calibration error, equipment error, signal registration error, calculation error, sampling error and dilution error (APHA, AWWA & WEF, 1998). To ensure quality control and quality assurance in analysis, it is vital to account for and quantify all possible errors associated with analysis, as these type errors are dependent on the utilized analysis technique. In this case, the

methods used were not all suitable for analysing highly concentrated brines. In general:

- The IC was suitable for sample solutions with EC < 100 μS/cm, whereas the case study brines had EC range of 6800 to 141000 μS/cm. In order to prepare the samples to the required EC range, dilution factors of up to 10 000 were required. Literature on how dilution factors affect quality control associated with IC when analysing highly concentrated samples was unavailable.

- The ICP-MS/AES was suitable for analysing brine sample with a concentration range of mid ppb's to 1000 ppm (1,000 mg/L) for major elements, such as sodium. The case study brines had a Na content range from 21149 to 70297 mg/L. The maximum dilution factor required was thus less than 100.

- Gran titration is a wet chemistry method and is theoretically not sensitive to high solute content. The method required dosing using HCl, which in this case resulted in salt precipitating out of the highly concentrated brine samples due to the common ion effect as the samples had a high Cl content. Diluting the samples was thus necessary and the dilutions did not exceed a dilution factor of 50.

- The TKN method is also a wet chemistry method and is theoretically not sensitive to high solute content. However, the H_2SO_4 acid mixture used for in the digestion step was highly concentrated and thus contained a high concentration of SO_4. This resulted in salt precipitating out of solution due to the common ion effect. Diluting the samples was thus necessary and the dilutions did not exceed a dilution factor of 20.

Due to the scope of this project, the two categories of error that were investigated were: (1) error due to disturbances caused by other components when analysing a particular component of choice and (2) dilution error.

4.3.3.1 **Methodology**

To test for the effects of multiple components on analytical method accuracy, synthetic brines and binary synthetic brines were prepared. Table 12 presents the brine salt make up for the multiple component error analysis. SB 1 had high carbonate content, SB 2 had high ammonia content and SB 3 had a high concentration of the major components found in the case study brines.

Table 13 presents the single salt make up brine for Cl, SO_4 and NO_3 anion error analysis. Table 14 presents the single salt make up brine for Na, Mg, K and Ca cation error analysis. Table 15 presents the single salt make up brine for carbonate and ammonia error analysis.

The dilution error analysis of each method was conducted as follows:

- In the case of IC, one set of samples was diluted to the required detectable EC level during preparation, while the other set was left to the operator to dilute to detectable conductivity level < 100 μS/cm. The two sets of results were then compared to the actual anion concentrations.

- In the case of ICP-MS/AES, a sample that required dilution and one that did not require dilution were prepared. The dilution was thus left to the operator to conduct to the detectible concentration level < 1000 ppm.

- In the case of Gran titration method, the samples were diluted by 5, 10, 20 and 50 factors of dilution. In the case of the TKN method the samples were diluted by 5, 10, 20 factors of dilution.

The labelling SB was used as an abbreviation for synthetic brine. The synthetic brines were prepared using the following salts NaCl (Cl and Na), Na_2SO_4 (SO_4), $NaNO_3$ (NO_3), Na_2CO_3 (CO_3), NH_4Cl (NH_4/NH_3).All synthetic solutions were prepared using MilliQ 10 MΩ deionised water and salt from Merck chemicals (Pty) Ltd and InivAR® chemicals.

Table 12: Multi-component make-up for general methods error analysis

Salt	Units	SB 1	SB2	SB3
NaCl	mg	22060	10240	77410
Na_2SO_4	mg	6820	15100	55240
Na_2HPO_4	mg	670	420	720
$NaNO_3$	mg	1080	1590	2990
NaBr	mg	320	340	1280
$NaHCO_3$	mg	11560	830	45940
NH_4Cl	mg	2230	7690	7690

Table 13: Single salt make-up for IC error analysis

Salt	Units	SB4	SB5	SB6
NaCl	mg	77410	-	-
Na_2SO_4	mg	-	55240	-
$NaNO_3$	mg	-	-	2180

Table 14: Single-salt make-up for ICP-MS/AES error analysis

Salt	Units	SB8	SB9	SB10	SB11	SB12
NaCl	mg	12710	6360	-	-	-
$MgSO_4$	mg	-	-	4950	-	-
KCl	mg	-	-	-	4770	-
$CaCl_2$	mg	-	-	-	-	2770

Table 15: Salt make-up for Gran titration and TKN error analysis

Salt	Units	SB 13	SB 14
$NaHCO_3$	mg	11560	-
NH_4Cl	mg	-	2230

The samples were prepared in triplicate to determine the standard deviation of each sample analysis. The relative error was the deviation of the obtained sample analysis concentration from the true known value and was defined as follows:

Relative error = [Absolute(Measured value – True value) ÷ True value] × 100 [16]

4.3.3.2 **Results and discussion**

IC error analysis

IC was able to detect all the required specific components in both the binary and multi-component synthetic brines. The general standard deviation of the IC anion analysis ranged from 0.02 to 0.97 % for all samples analysed. The IC thus had reasonably good reproducibility in analysis results. All IC measurements were lower than the true anion concentrations, thus giving underestimates. Figure 21, Figure 22 and Figure 23 illustrate the Cl, SO_4, and NO_3 concentrations respectively of diluted and non-diluted samples, relative to the actual concentrations. The diluted and non-diluted sample results were relatively similar and had a small deviation from the actual concentration. The relative error of the

multi-component brine system analysis did not differ much from that of the single salt system brine analysis.

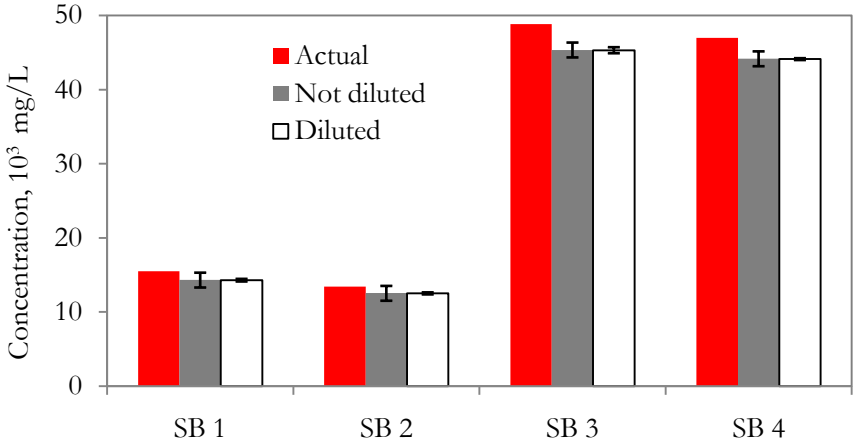

Figure 21: IC synthetic brine analysis results for Cl

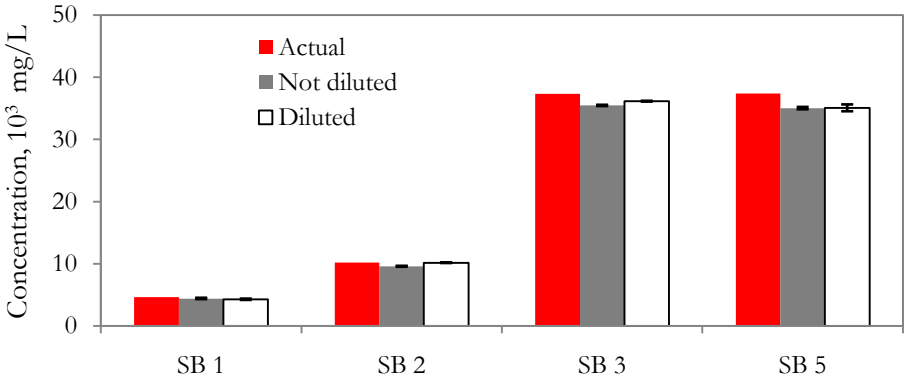

Figure 22: IC synthetic brine analysis results for SO_4

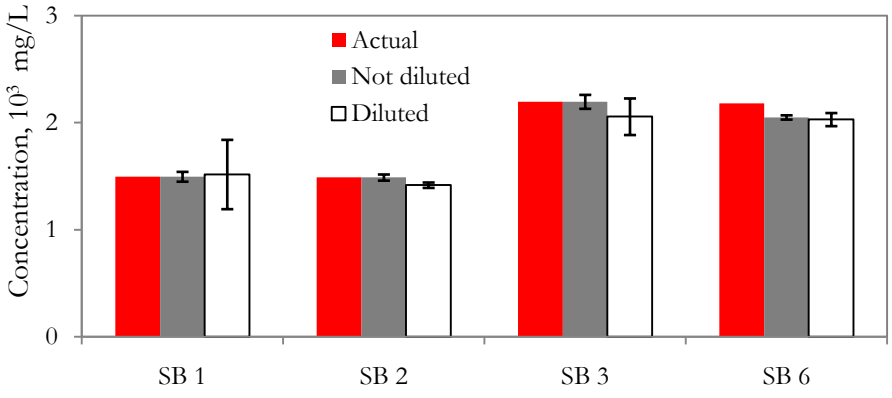

Figure 23: IC synthetic brine analysis results for NO_3

ICP-MS/ICP-AES error analysis

The ICP-MS/AES was able to detect all the required specific components in both the binary and multi-component synthetic brines. The general standard deviation of the ICP-MS/AES cation analysis ranged from 0.03 to 0.98 %. The ICP-MS/AES thus had reasonably good reproducibility in analysis results. All measurements were lower than the true cation concentrations, thus giving underestimates. Figure 24 illustrates the obtained Na results. The relative error of the Na analysis ranged from 3.9 to 9.2 %. The relative error of the multi component brine system analysis did not differ much from that of the single salt system brine analysis. Figure 25 illustrates the relative error of Mg, Ca and K. The relative errors of Mg, Ca and K were 11, 9.7, and 9.33 % respectively.

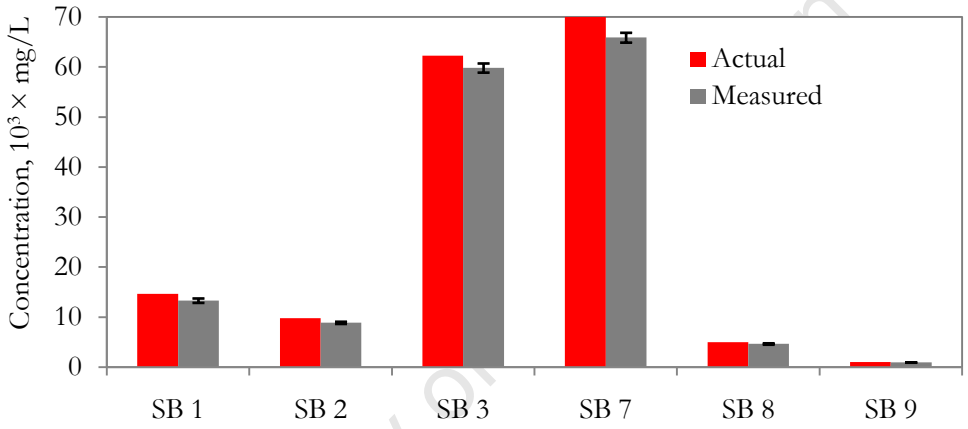

Figure 24: ICP-MS/AES synthetic brine analysis relative error for Na

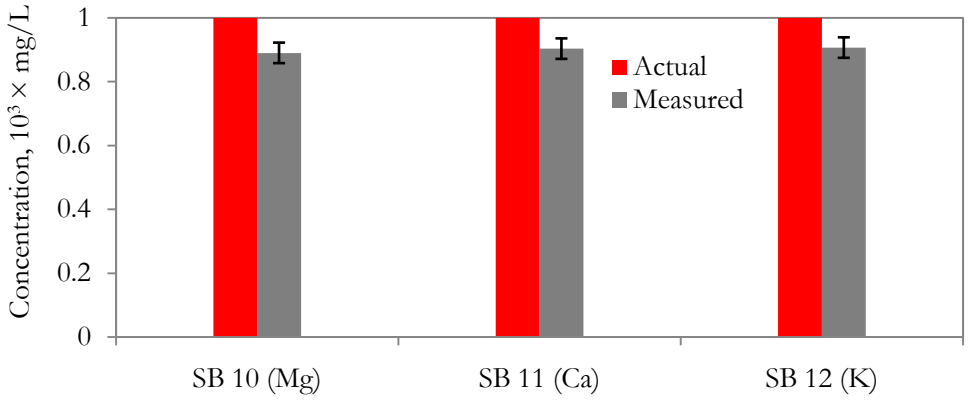

Figure 25: ICP-MS/AES synthetic brine analysis relative error for Mg, Ca and K

Gran titration error analysis

The general standard deviation of the Gran titration method analysis ranged from 0.00 to 0.02 %. All

measurements were lower than the true concentrations, thus giving underestimates. Figure 26 illustrates the obtained HCO_3 analysis results of the multi-component synthetic brines. The relative error ranged from 9.6 to 10.2 %. Figure 27 illustrates the relative error analysis as a function of dilution error. The relative error ranged from 9.1 to 10.1 %. The dilution factors did not cause much error. The multi-component and single salt system brine analysis results were identical. The method was not affected by the dilution factors or the multiple components in the brine matrix.

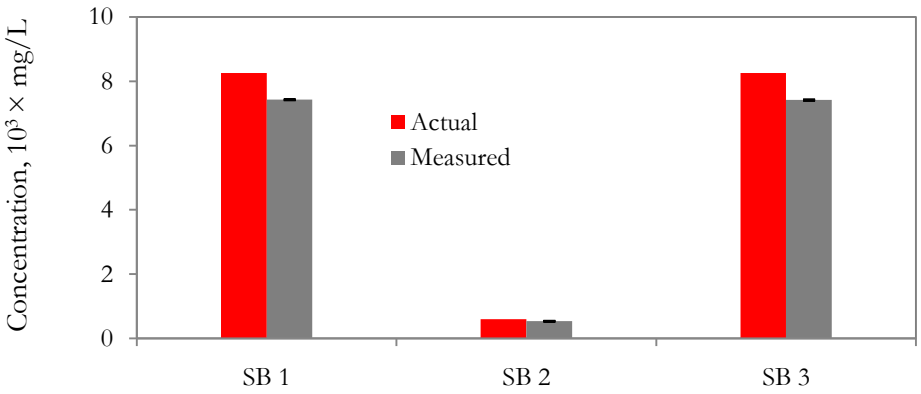

Figure 26: Gran titration synthetic brine analysis results for HCO_3^-

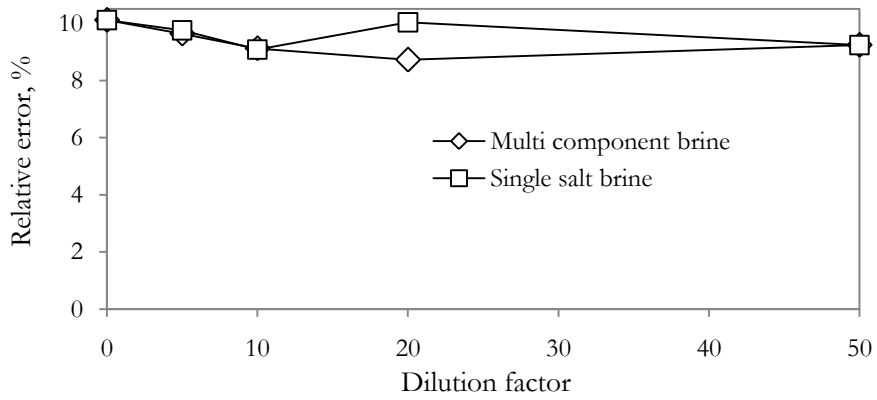

Figure 27: Gran titration synthetic brine analysis relative error vs. dilution factor

The general standard deviation of the TKN method analysis ranged from 0.01 to 0.02 %. All measurements were lower than the true concentrations, thus giving underestimates. Figure 28 illustrates obtained NH_4 analysis results of the multi-component synthetic brines. The relative error ranged from 6.85 to 7.68 %. Figure 29 illustrates the relative error analysis as a function of dilution error. The relative error ranged from 9.34 to 10.82 %. The dilution factors did not cause much error. The multi-component and single salt system brine analysis results were relatively identical. The

method was not affected by the dilution factors or the multiple components in the brine matrix.

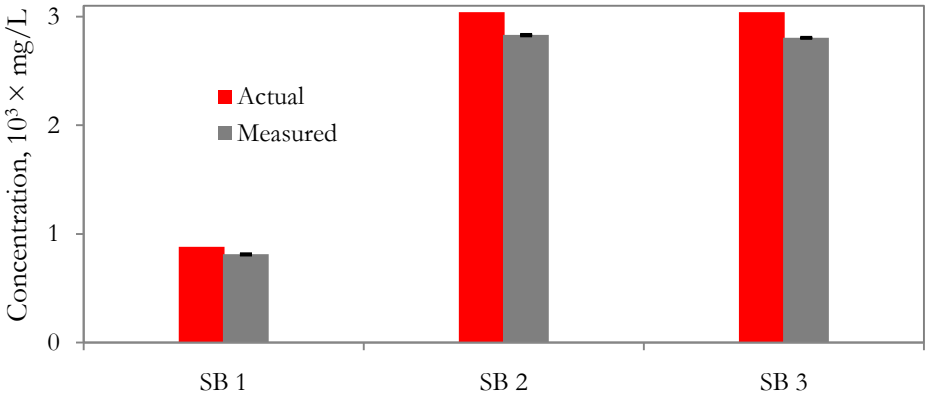

Figure 28: TKN synthetic brine analysis results for NH_4^+

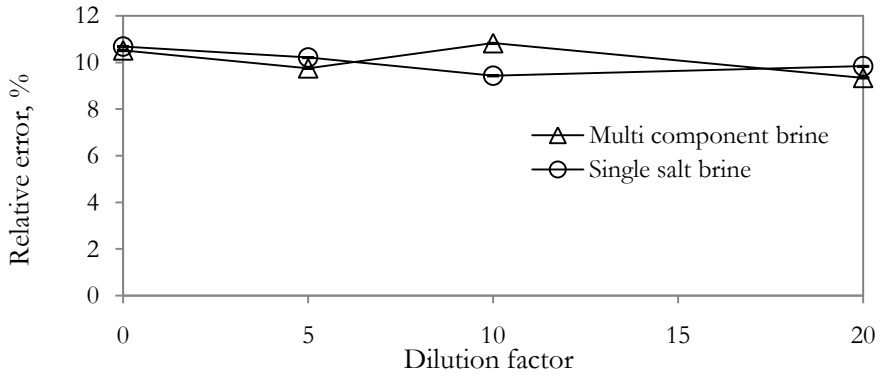

Figure 29: TKN synthetic brine analysis relative for NH_4^+ vs. dilution error

4.3.4 Thermodynamic modelling results

Table 16 presents the summarised brine analysis results that were used as the basis of the thermodynamic modelling input data.

The charges were balanced by adding the dominant cation ion or anion, and this is called the dominant-ion method. The dominant-ion method is usually the preferred method to balance the electroneutrality since the dominant ion usually has the largest absolute error associated with the measurement. Thus adding a small amount does not affect the measured value all that much. The other method that can be used is called the make-up ion method. The make-up ion method allows the user to pick any ion, positive or negative, in which to balance the electroneutrality of the solution. In

many cases this chosen ion may be the same as the dominant ion.

Table 16: Summarised industrial brine analysis results used for thermodynamic modelling

Component	Units	MTB	MTM	GSX
pH		12.8	9.8	7.0
Conductivity	mS/cm	129	141	68
Density	g/cm^3	1.07	1.15	1.06
CO_3	mg/L	8261	21202	-
HCO_3	mg/L	-	11619	390
NH_3	mg/L	876	86	-
NH_4	mg/L	-	18	54
PO_4	mg/L	450	475	55
SO_4	mg/L	4613	37363	29920
NO_3	mg/L	788	2175	785
NO_2	mg/L	-	-	395
Cl	mg/L	13375	46963	11135
Br	mg/L	250	988	85
Na	mg/L	31353	70297	21149
Mg	mg/L	-	-	208
Si	mg/L	94	251	44
K	mg/L	33	110	2161
Ca	mg/L	4	5	707
Fe	mg/L	-	-	-
Cd	mg/L	1	2	-
Ni	mg/L	-	9	1

The charges were balanced by adding the dominant ion, either a cation ion or an anion and this is called the dominant-ion method. The dominant-ion method is usually the preferred method to balance the electroneutrality since the dominant ion usually has the largest absolute error associated with the measurement. Thus adding a small amount does not affect the measured value all that much. The other method that can be used is called the make-up ion method. The make-up ion method allows the user to pick any ion, positive or negative, in which to balance the electroneutrality of the solution. In many cases this chosen ion may be the same as the dominant ion.

The adjustment of pH was made by adding HCl or NaOH depending on the fixed pH value of the stream. The model requires and enables the user to select a strong acid and base to titrate to the specified pH end point. HCl and NaOH are strong acid and base solutions that are generally used, but the user has an option of choosing any strong acid or base. The pH values of the streams were fixed at

the brine pH values presented in Table 16. The obtained case study brine charge balance is presented in Table 17. None of the streams were balanced. The ion imbalances ranged from 0.06 to 0.08 eq/L.

Table 17: The obtained case study brine charge balance

Property	Units	MTB	MTM	GSX
Cation	eq/L	1.36	3.06	1.03
Anion	eq/L	-1.29	-3.26	-0.97
Imbalance	eq/L	0.08	-0.2	0.06
% Imbalance	%	5.15	6.13	5.83
Dominant ion		Cl^-	Na^+	SO_4^{2-}
Added amount	mg/L	2,783	4,522	3,037
Difference	%	8.9	6.4	10.2

The basic metallurgical brine had excess positive charge and thus 2783 mg/L dominant anion Cl^- (an addition of 8.9 % from the entered value) was added to balance the charge. The mixed metallurgical brine had excess negative charge and thus 4522 mg/L dominant cation Na^+ (an addition of 6.4 % from the entered value) was added to balance the charge. The gasification brine had excess positive charge and thus 3037 mg/L dominant anion SO_4^{2-}(an addition of 10.2 % from the entered value) was added to balance the charge.

Ion imbalance should be within 5 % when a proper analysis protocol is executed and if it exceeds 10 % then there is a major error in the analysis. Either the analysis was not well conducted or there are ions that have not been accounted for in the analysis (Pulles et al., 1996). From the case study brines, the ion imbalance ranged from 5.15 to 6.13 % and less than 10 %.

A possible reason for the imbalance could have been due to the time-span it took to conduct the analysis of these brines. pH and alkalinity were not analysed within the time limit. The shortage could have been caused by not determining the pH and alkalinity on site. Dissolved $HCO_3^-$is in equilibrium with H_2CO_3 which is also in equilibrium with dissolved CO_2 according to the following expression:

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3 \leftrightarrow CO_2\,(l) + H_2O \leftrightarrow CO_2\,(g) + H_2O \quad [17]$$

It is not known to which extent this equilibrium reaction could have shifted towards the right, favouring the formation of CO_2 from HCO_3^- bearing in mind that the gas ↔ liquid equilibrium is dependent on the partial pressure of the gas. This phenomenon could have resulted in the deficiency

of anion in the water matrix.

As seen in the previous section, the utilized analysis techniques had global general methods relative error range of 3.90 to 10.82 % associated with them, and that thus could have resulted in the deficiency of anions in the basic metallurgical and gasification brine and cations in the mixed metallurgical brine.

Chapter 5 Brine Analysis Sensitivity on EFC

5.1 Introduction

Chapter 2 reviewed the accumulation of inorganic hypersaline brines in South Africa and how this has negative environmental effects. Lewis et al. (2010) proposed a protocol for treating industrial brine using eutectic freeze crystallisation (EFC). The principle steps were brine sampling and storage, brine characterisation, thermodynamic modelling, experimental verification and EFC reactor design. It was seen how all the these steps are interdependent and how the failure of conducting proper brine sampling and storage affects the overall sample analysis results, which in turn affect thermodynamic modelling results.

The practice of a method of conducting brine analysis that excludes the carbonate analysis most often results in great ion imbalances and the technique that is mostly used to make up for the imbalance would be by adding the dominant cation or anion to balance the negative or positive charge. From the literature review, it was seen that ion imbalance in water analysis is often caused by the exclusion of the carbonate system, among other factors. The aim of this chapter was to illustrate the effects of not including the carbonate system in the analysis on the prediction of salt and water recovery using cooling crystallisation. EFC is a combination of cooling and freeze crystallization and so the observed results apply to EFC.

5.2 Methodology

The prediction of salt and ice crystallization in the case study brines was conducted using OLI Stream Analyser 3.0.10 software. The software was capable of accurately simulating aqueous chemistry at high ionic strengths. The salt and ice crystallisation predictions were conducted over a temperature range of 25 ^{o}C to -25 ^{o}C. Therefore, the mixed solvent electrolyte (MSE) database was used, which uses the Helgeson direct method and thus enables the model to conduct modelling at temperatures as low as -200^{o}C.

5.3 Results and discussion

Figure 30 presents the basic metallurgical brine salt and ice crystallization prediction using cooling crystallisation, with carbonate system excluded. Figure 31 presents the basic metallurgical brine salt and ice crystallization prediction using cooling crystallisation, with carbonate system included. Ice

crystallizes first at 0 °C in both scenarios. Salt crystallised out at -5 °C in both cases. However when the carbonate system was included, a mixed $Na_2CO_3.10H_2O$-$Na_2SO_4.10H_2O$ salt was formed, compared to the single $Na_2SO_4.10H_2O$ salt formed when the carbonate system was excluded. $NaCl.2H_2O$ single salt crystallised out of solution at -20 °C in both scenarios.

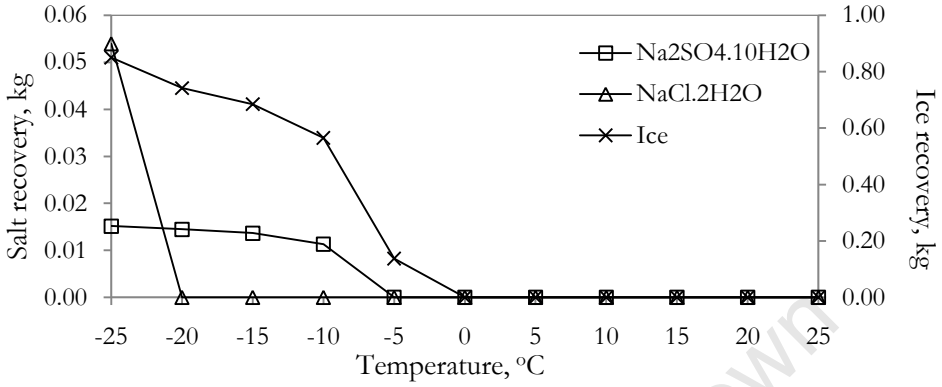

Figure 30: MTB brine salt and ice crystallisation prediction using cooling crystallisation (carbonate system excluded)

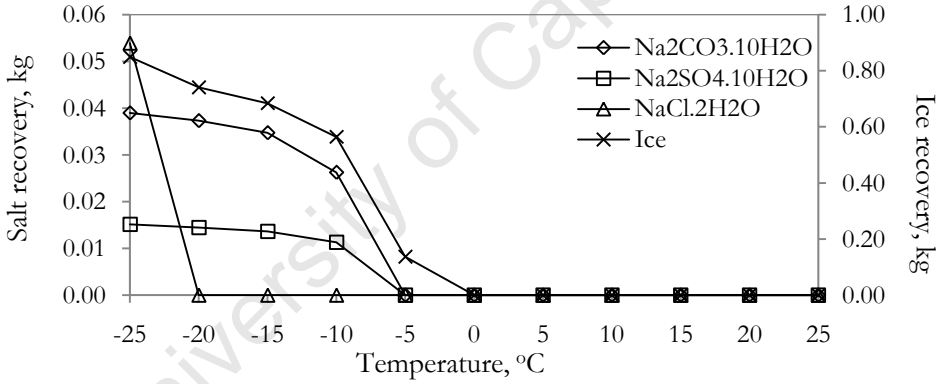

Figure 31: MTB brine salt and ice crystallisation prediction using cooling crystallisation (carbonate system included)

Figure 32 presents the mixed metallurgical brine salt and ice crystallization prediction using cooling crystallisation, with carbonate system excluded. Figure 33 presents the mixed metallurgical brine salt and ice crystallization prediction using cooling crystallisation, with carbonate system included. Due to the high salinity of the brine, $Na_2SO_4.10H_2O$ salt crystallised out of solution at 15 °C in both scenarios. $Na_2CO_3.10H_2O$ was the next to precipitate out of solution in the case where carbonate was included. Ice and $Na_2Cl.2H_2O$ were next to precipitate out of solution at -5 and -20 °C respectively in both scenarios.

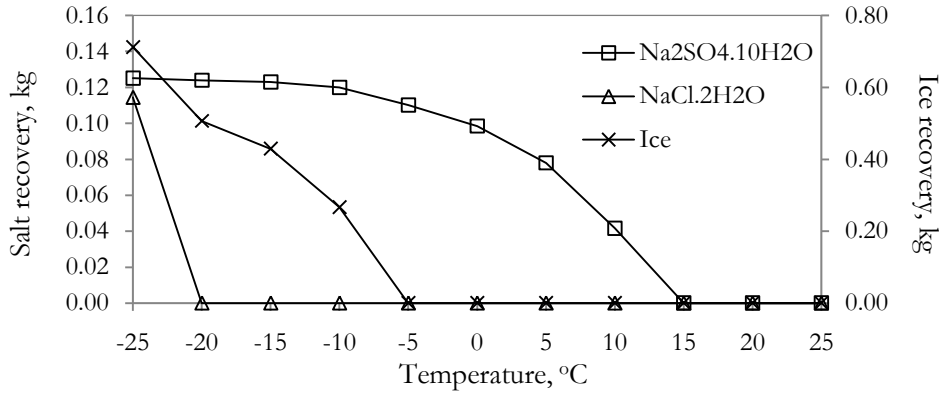

Figure 32: MTM brine salt and ice crystallisation prediction using cooling crystallisation (carbonate system excluded)

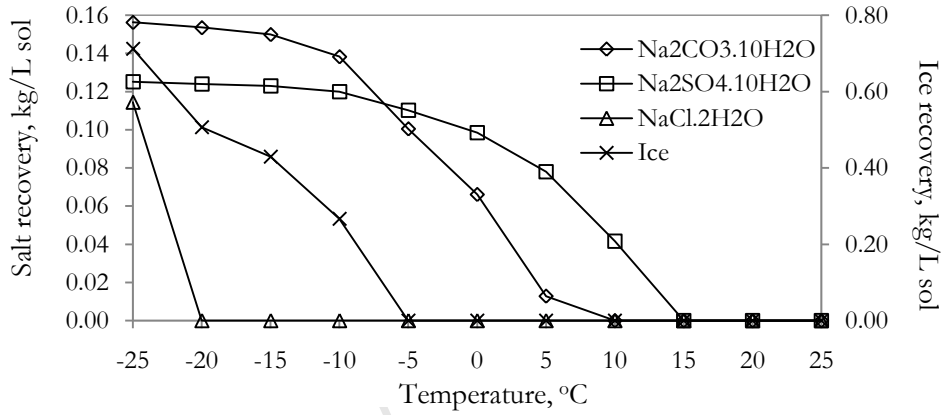

Figure 33: MTM brine salt and ice crystallisation prediction using cooling crystallisation (carbonate system included)

Figure 34 illustrates the gasification brine salt and ice crystallization prediction using cooling crystallization. $Na_2SO_4.10H_2O$ single salt crystallized out of solution at 5 °C. This was because the brine sample was relatively dilute and rich in sulphate ions. The single $Na_2SO_4.10H_2O$ salt crystallized out of solution at -5 °C. No carbonate salt precipitated out of solution because the brine had little carbonate content. $NaCl.2H_2O$ single salt crystallised out of solution at -20 °C in both scenarios. However, $NaCl.2H_2O$ yield was relatively lower than $Na_2SO_4.10H_2O$ yield.

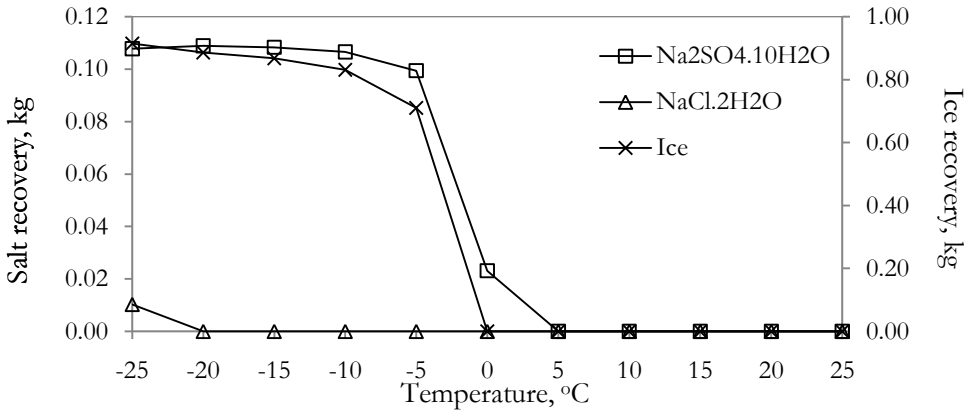

Figure 34: The GSX brine salt and ice crystallisation prediction using cooling crystallisation

The pH, salinity and composition of industrial brines generally depend on the industrial process as seen from the case study brines. These factors play an important role in reactor design, which is generally dependant on modelling. The conducted sensitivity analysis showed that not accounting for carbonate system results in not obtaining the correct information about the characteristics of salts formed in different temperature intervals when applying EFC to treat the case study brines. *Note that in this case carbonate was used as an example*. There are contaminants which should be expected, for example in the basic metallurgical brine case, a mixed $Na_2CO_3.10H_2O$-$Na_2SO_4.10H_2O$ salt was predicted to crystallise out of solution as opposed to a $Na_2SO_4.10H_2O$ forming when excluding carbonate system. This information is very important in reactor design and EFC experimental processes.

In multi-component aqueous systems, some salts crystallize out at similar eutectic temperatures. In order to overcome the formation of a contaminated salt, seeding is used to induce crystallisation of the specific desired salt. This theoretically results in the recovery of a pure salt as opposed to a mixed salt formed when using evaporative crystallisation, which is one of the principle advantages of using EFC over evaporative crystallization. Having a full brine analysis (1) favours accurate EFC modelling and accurate salt and ice crystallization prediction. (2) It enables one to have an idea of when to use seeding for the selective crystallisation of the desired salt. (3) It favours the selection of the ideal operating conditions, such as cooling rate and preparation of sample concentration. (4) It enables one to design a reactor using the appropriate reactor material to avoid unnecessary damages to the reactor, such as corrosion. (5) From a safety point of view; it enables one to wear the correct protective gear or material with full knowledge of all possible hazardous contaminants in the brine solution.

As Musvoto and Ramphao (2007) put it: the provision of novel and viable solutions is highly

dependent on research and development, which encompasses accurate wastewater characterisation and modelling for the design of wastewater treatment plants or extension of existing plants. EFC is in its developmental stages. Like any other water treatment method, it was shown that EFC is highly sensitive to brine characterisation. Well executed brine characterisation practices will enable quality research and development of this novel technology.

Chapter 6 Conclusions and Recommendations

The following conclusions were made based on the findings:

- The principle steps in brine characterisation and modelling were brine sampling and storage, brine analysis and thermodynamic modelling. These principle steps were dependent on each other. Reliable thermodynamic modelling was dependant on a comprehensive brine analysis program, which in turn was dependant on a well-executed brine sampling and storage program.

- The developed industrial brine characterisation and modelling protocol was successful when applied to the inorganic hypersaline case study brines.

- Na, Cl, SO_4, alkalinity and ammonia were the major contaminants of the case study brines. The presence and levels of these components were industrial process dependent.

- The carbonate system completely characterised the alkalinity of the case study brines as it had a 97 – 99 % contribution towards the total alkalinity. Total hardness was insignificant due to the extremely low levels of Ca and Mg contents.

- The inclusion of the carbonate system in the brine analysis contributed towards a reduction in the ion imbalance. This was consistent with literature review on the effects of carbonate system on ion imbalance.

- Multiple components and dilution factors did not affect the reproducibility of the analysis results when conducting methods error analysis.

- The cooling crystallization thermodynamic simulation was highly dependent on a well-executed brine characterisation program. The inclusion of carbonate in the thermodynamic simulation resulted in the prediction of $Na_2CO_3.10H_2O$ salt forming, which contaminated $Na_2SO_4.10H_2O$ salt. This was useful information as it meant that seeding would be necessary to selectively form a pure $Na_2SO_4.10H_2O$salt using EFC. This illustrated the importance of conducting a full brine analysis when characterising industrial inorganic hypersaline brine systems.

The following recommendations were made:

- Due to the dependency of thermodynamic modelling on a comprehensive sample analysis program, it is crucial to request that the company from which the brine is obtained conduct some brine analysis. This thus gives an indication of the type of analysis that should be conducted upon arrival of the brine at the laboratory. It also means that pH and alkalinity measurements would be more accurate based on the recommended analysis time limit.

- When conducting analysis on this scale, it is crucial to obtain the process flowsheet diagram of the industrial process. This provides a broader picture of all possible contaminants in the brine matrix. This also enables one to choose the relevant analytical methods for analysing for it known contaminants. It is also crucial to obtain the sampling program used. This enables one to conduct error analysis associated with sampling.

- It is crucial to adhere to the recommended sample preservation and maximum holding period.

- The search for effective analytical techniques that are able to analyse highly concentrated industrial brines with extremely high and low pH values should continue.

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Chapter 8 Appendix

8.1 TKN Procedure (EPA, 1999)

8.1.1 Reagents

Mercuric sulphate ($HgSO_4$)

Dissolve 40 g red mercuric oxide (HgO) in 250 ml of H_2SO_4:5 water (50 ml: 250 ml) and dilute to 800 ml with distilled water.

Sulphuric acid (H_2SO_4) – mercuric sulphate ($HgSO_4$) – potassium sulphate (k_2SO_4) solution

Dissolve 333.75 g K_2SO_4 in 1800 ml distilled water and add 500 ml concentrated H_2SO_4. Add 62.5 ml $HgSO_4$ solution and dilute to 2500 ml. This reagent crystallizes at temperatures lower than 14°C.

7M H_2SO_4 solution

Dilute 485 ml concentrated H_2SO_4 (>98%) in distilled water and make up to 2500 ml with distilled water.

Digestion mixture

Mix the two solutions made up in 2.2 and 2.3 above to give 5000 ml of digestion mixture.

Mixed indicator

Mix the two volumes of 0.2% methyl red in 95% alcohol with 1 volume of 0.2% methylene blue in 95% alcohol. This solution must be made fresh every 30 days.

Boric acid (H_3BO_3)

Dissolve 100g H_3BO_3 in distilled water. Add 100 ml of mixed indicator (or 40 ml blue and 80 ml red), and dilute to 5000 ml.

0.001M H_2SO_4 solution

Prepare a stock solution of 0.1M H_2SO_4 by diluting 2.8 ml concentrated H_2SO_4 to 1000 ml. Dilute 200 ml of the 0.1M H_2SO_4 stock solution to 1000 ml with distilled water to give a 0.02M stock solution.

Dilute 100ml of the 0.02M H_2SO_4 stock solution to 2000 ml to give an approximately 0.001M H_2SO_4 solution.

Sodium hydroxide (NaOH) – sodium thiosulphate solution ($NaS_2O_3.5H_2O$)

Dissolve 500 g NaOH and 25 g $Na_2S_2O_3.5H_2O$ in distilled water and make up to 1000 ml. This procedure is done in a plastic container as the reaction is exothermic.

8.1.2 Procedure

1. Pipette a 5ml influent sample or a 10 ml reactor or effluent sample into a 30 ml micro Kjeldahl flask. Add 10 ml digestion mixture (2.4) and 3 glass beads (approximately 3 mm diameter).
2. Digest the sample mixture on heating element until the sample is clear, and heat for another 20 minutes.
3. Connect the Kjeldahl flask to the micro steam distillation apparatus and allow to cool for approximately 30 minutes.
4. Pipette 25 ml of H_3BO_3 solution (2.6) into a 100 ml Erlenmeyer flask and place in position on the steam distillation apparatus with the nozzle of the condenser immersed in the solution.
5. Add about 10 ml of distilled water to the contents of the Kjeldahl flask to dissolve the sediment.
6. Add 7 ml of NaOH solution (2.9) to the contents of the Kjeldahl flsk via the top opening of the steam distillation apparatus, and immediately seal the apparatus by placing the steam line in position.
7. Steam and distil until the volume of the H_3BO_3 solution in the Erlenmeyer flak is approximately 50 ml.
8. Titrate the contents of the Erlenmeyer flask for the sample with standardized 0.001M H_2SO_4 solution (2.8)
9. Calculation:

$TKNmgN/L = (a \times M) \div A$

Where a = ml 0.001M H_2SO_4 for sample; M = 0.001M H_2SO_4 concentration; A = ml sample volume

8.2 Gran titration

8.2.1 Method Theory

The extended Gran method theory is summarized from (Loewenthaland co-workers, 1989).

The Gran method includes the titration of a carbonate subsystem to H_2CO_3* equivalent point (i.e. pH≤ 4.5) using a strong acid, thus having data in the 3.3 ≤ pH ≤ 3.8 range, V_E is the unknown volume of strong acid used to reach an equivalent H_2CO_3*/$H_2PO_4^-$ /NH_4^+/HAc solution. The following expression gives the relationship between the H_2CO_3*/$H_2PO_4^-$ /NH_4^+/HAc alkalinity and V_E.

$$H_2CO_3^*/H_3PO_4/NH_4^+/HAc \text{ alkalinity} = V_E C_a/V_s = T.Alk \quad [18]$$

Having added V_x of standard acid, the two equations that can be formulated for total alkalinity in terms of species subsystems, and in terms of V_E and V_S are as follows:

$$T.Alkalinity_x = -[H_3PO_4]_x + [Ac^-]_x - [H^+]_x \quad [19]$$

$$T.Alkalinity_x = \frac{V_E C_a}{V_S+V_x} - \frac{V_x C_a}{V_S+V_x} \quad [20]$$

Equating and simplifying the two equations yields the following expression:

$$C_a(V_E - V_x) = (-[H_3PO_4]_x + [Ac^-]_x - [H^+]_x)(V_s - V_x) \quad [21]$$

Where:

$$[H_3PO_4]_x = \frac{10^{-pH_x}}{10^{-pH_x}+10^{-pK`_1}} \cdot \frac{P_T V_S}{V_s+V_x} \quad [22]$$

$$[Ac^-]_x = \frac{10^{-pK`_a}}{10^{-pH_x}+10^{-pK`_a}} \cdot \frac{A_T V_S}{V_s+V_x} \quad [23]$$

$$[H^+]_x = \frac{10^{-pH_x}}{f_m} \quad [24]$$

$K`_a$ and $K`_{p1}$ are acetate and first phosphate apparent weak acid dissociation constants respectively. A more simplified and useful mode of presenting the above equations is by the Gran function F_{1x}:

$f_m C_a(V_E - V_x) = -O_x - Q_x + R_x = F_{1x}$ [25]

Where

$O_x = (10^{-pH_x})(V_s + V_x)$ [26]

$$Q_x = \frac{f_m P_T 10^{-pH_x}}{10^{-pH_x} + 10^{pK`_{p1}}} . V_s$$ [27]

$$R_x = \frac{f_m A_T 10^{pK`_a}}{10^{-pH_x} + 10^{pK`_a}} . V_s$$ [28]

F_{1x} is obtained by substituting V_x and corresponding pH_x into the above equation. A linear relationship is obtained when plotting V_x vs. F_{1x}. By linear extrapolation, $F_{1x} = 0$ is obtained which gives $V_E = V_x$, and V_E is then used to calculate H_2CO_3* total alkalinity from the following expression:

H_2CO_3*/H_3PO_4/NH_4^+/HAc alkalinity = Alk H_2CO_3* + Alk H_3PO_4 + Alk NH_4^+ + Alk HAc + Alk H_2O [29]

Where

$$\text{Alk } H_3PO_4 \approx \frac{P_T 10^{-pK`_{p2}}}{10^{-pH_0} + 10^{-pK`_{p2}}}$$ [30]

$$\text{Alk HAc} = \frac{A_T 10^{-pK`_a}}{10^{-pH_0} + 10^{-pK`_a}}$$ [31]

$$\text{Alk } NH_4^+ = \frac{N_T 10^{-pK`_n}}{10^{-pH_0} + 10^{-pK`_n}}$$ [32]

$$\text{Alk } H_2O = 10^{pH_0 - pK`_W} - \frac{10^{-pH_0}}{f_m}$$ [33]

Rearranging equation 13 and making Alk H_2CO_3* the subject of the formula results in the following equation:

Alk $H_2CO_3^*$ = $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alkalinity – Alk H_3PO_4 – Alk NH_4^+ – Alk HAc – Alk H_2O [34]

Finally the total carbonate concentration, C_T, is obtained from the following expression:

$$C_T = \frac{1+10^{pK`_{c1}-pH_0}+10^{pH_0-pK`_{c1}}}{1+2\times10^{pH_0-pK`_{c2}}}.\text{Alk}\,H_2CO_3^* \quad [35]$$

To verify the accuracy of the extended Gran method (Loewenthal, Ekama & Marais 1989) conducted a test on the carbonate, acetate, phosphate, ammonium weak acid subsystem. They found that the measured C_T and calculated C_T agreed with 2% of the expected value from the input carbonate system.

8.2.2 Procedure (Loewenthal and co-workers, 1989)

- Calculate the monovalent ion activity coefficient f_m from the following Davies (Butler, 1964) expression:

$$logf_m = -1.825\times10^6(78.3T)^{-1.5}\times Z_m^2\left(\frac{\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}}-0.3\mu\right)$$

  Where:

  μ = $1.68.10^{-4}$.SC = ionic strength, in mS/m; SC = specific conductance, in mS/m;
  Z_m = 1 for monovalant charge; T = temperature in Kelvin

- Calculate the apparent dissociation constants for the phosphate and acetate systems at reference temperature.
- Calculate the contributions of the three terms O_x, Q_x and R_x of the extended Gran function from pH_x and V_x observations using equations 26, 27 and 28 respectively.
- Plot F_x vs. V_x from the data obtained and extrapolate the linear section of the plot to F_x = 0.
- Determine the volume of acid added to reach the equivalent solution V_E, from the graph; this is given by the intersection point of the extrapolated line with the horizontal axis.
- Calculate the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity from:
  $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alkalinity = V_EC_a/V_s = T.Alk [36]
  Where C_a = strong acid molar concentration, in mol/l; V_S = sample volume, in ml

- Determine Alk H_3PO_4, Alk HAC, Alk NH_4^+ and Alk H_2O from equation 30 – 33.
- Calculate Alk $H_2CO_3^*$ from equation 34.

- Calculate carbonate concentration, C_T, from equation 35.

Generally the indications are that very accurate results can be obtained with the method, provided the parameters and NH_3, PO_4 and Ac concentration are highly accurate.